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Project Termination Report

G. B. Parker

September 1979

Prepared for the U.S. Department of Energy
Fuel Cycle Program Office
Under Contract EY-76-C-06-1830
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Pacific Northwest Laboratory
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ABSTRACT

This report describes work to examine the use of solid sorbents to remove tributyl phosphate vapors from commercial nuclear fuel dissolver and vessel vent off-gas streams. Tributyl phosphate has been shown to have a deleterious effect on silver loaded solid sorbents used to remove airborne iodine from these off-gas streams.

The work described was conducted in four phases, the fourth phase incomplete: the first phase was to select commercial inorganic solid sorbents from manufacturer's literature that would indicate their effectiveness in removing airborne organophosphates. The second phase was to screen these materials in the laboratory in short term TBP loading experiments to assess their effectiveness to trap small amounts of TBP. Quantitative analysis techniques were developed as part of this phase. The third phase was long term parametric TBP loading experiments using short columns of the selected materials from phase 2 to determine the capacity of the materials for TBP. The final phase was laboratory demonstration experiments to study the effectiveness of the most successful materials from phase 3 as a protective media for the iodine sorbent in a simulated off-gas cleaning system containing airborne iodine and commercial iodine sorbent.

The study identified one commercially available alumina catalyst which proved to be an effective, superior sorbent for TBP. Adjunct to this main objective, analytical and procedural methods were developed for handling and measuring low concentrations of TBP. Results of the experiments to demonstrate the protection of silver-impregnated mineral beds raised an important question, yet unanswered, regarding the necessity of removing TBP from process streams for some silver-impregnated beds to attain full stoichiometric removal of iodine. The study was terminated due to funding withdrawal before this and other questions were answered.

SUMMARY

A research project was undertaken to develop a process to remove tributyl phosphate (TBP) vapors from off-gas streams of commercial nuclear fuel reprocessing plants. Low concentrations of TBP in process off-gas streams have a deleterious effect on the retention capacity of silver loaded sorbent beds to remove airborne iodine from these off-gas streams. The project was to identify a TBP removal process, study the process in laboratory scale experiments, test the process from a full scale reprocessing plant operating either at Savannah River or Hanford. As part of this final task, a quantitative measurement of TBP vapor concentration would be made in the various off-gas streams of the operating plants.

The project was initiated in April, 1976 and was terminated in September, 1978 before all tasks could be completed. The shift away from commercial nuclear fuel reprocessing as an option for spent fuel was the major contributing factor for suspension of research in this area. The program was scheduled to be completed at the end of fiscal year 1980. A significant amount of laboratory research was accomplished, however, during the two years of effort. This research could be set in motion again from the point of termination with little impact from the work stoppage.

Several solid sorbent materials that indicated properties for trapping organophosphates or similar compounds were selected for use in short term airborne TBP loading experiments in the laboratory. Candidate materials for screening studies included silica gel, alumina, acid-treated clay, diatomaceous earth, and zeolite molecular sieves. The materials were initially studied in the laboratory using a packed stainless steel column segment at 100°C with 400 to 1000 mg/m^3 TBP vapor flowing at 162 mℓ/min. Three materials that retained >95% of the TBP, designated A, D, and L, were identified to be used in further parametric experiments.

Quantitative analysis of airborne TBP was initially performed by a standard NIOSH method used for pesticides. This involved trapping the TBP by sparging through a known volume of ethylene glycol over a known time period. The TBP was extracted from the glycol with hexane, the volume

reduced and liquid aliquots injected into a gas chromatograph equipped with a flame ionization detector. This method was later modified by using hexane in a cold trap in place of the glycol.

In later experiments, a commercially available real time instrument was acquired for TBP analysis. The instrument used a patented flame photometric detector and could measure concentrations as low as 0.1 mg/m^3 TBP. The instrument, a Meloy Laboratories PA460, was modified before use. A calibration system was developed for this instrument which also served as a TBP generation apparatus used in the parametric experiments summarized below.

A potential alternative method of analysis was explored which involved the use of laser technology. Laser analysis was considered because it could be used remotely to measure TBP vapor (and possibly other constituents) in actual reprocessing off-gas streams. A special diode was acquired for use in a helium cooled laser, and an optoacoustic sensing technique was chosen for use. The funding for this task was withdrawn before any experimentation could begin.

Parametric studies on the three materials (A, D, and L) from the screening studies were conducted. These studies used an apparatus consisting of material packed in 2.5 cm diameter glass columns through which airborne TBP vapor was metered. Conditions of air flow rate and TBP concentration were varied to assess the effects of these parameters on TBP breakthrough and retention.

Of the materials studied, material A, an alumina catalyst, had the greatest TBP retention in 3.8 cm deep beds of material. The retention capacity was 30 times greater than 3.8 cm of a crushed form of material D, which had the next highest retention capacity.

The final phase of the work described in this report was demonstration of the effectiveness of material A to remove TBP in a bench scale unit which simulated a typical "cold" reprocessing off-gas stream. This study consisted of several experiments using two stainless steel columns. The columns were made of 2.5 cm diameter segments packed 5 cm deep with solid

sorbent material. One column contained selected commercial iodine sorbent only, the other contained two segments of material A (the TBP sorbent) followed by several segments of the same commercial iodine sorbent.

During the experiments, an air stream containing water vapor, 30% TBP in NPH (normal paraffin hydrocarbon) vapor and methyl iodide (the source of iodine) was fed to the two columns simultaneously which were heated to 130°C-135°C. The breakthrough of methyl iodide was followed throughout the column segments by gas chromatographic analysis. By comparing the methyl iodide retention in the two columns, the effectiveness of the TBP sorbent was ascertained.

Two experiments were run using a commercial silver impregnated silica gel iodine sorbent (7 wt% Ag and 14 wt% Ag). The first experiment, using the 7 wt% sorbent, and TBP concentration of 80 mg/m^3, indicated that the TBP did not reduce the iodine retention of the sorbent. The iodine retention was stoichiometric at saturation (100% breakthrough) in two 5 cm segments of iodine sorbent from both columns.

Results of the second experiment using the 14% Ag sorbent and TBP concentration of 500 mg/m^3, also indicated that the TBP did not reduce the iodine retention capacity. The iodine retention was stoichiometric in segments from both columns, which indicated 100% breakthrough (saturation).

A third experiment was conducted using a commercially available 18 wt% substituted mordenite material. Two columns were again used, one containing two segments of material A. Concentration of TBP was 500 mg/m^3. Results showed that TBP reduced the capacity of the unprotected column by 60% compared to the column protected by two segments (10 cm) of material A.

The final experiment using the demonstration unit was designed to assess the effects of NO_2 on the iodine sorbent. Two columns of 5 segments (25 cm) of the 7 wt% iodine sorbent only were loaded with methyl iodide in air containing 500 mg/m^3 TBP. One column was removed after approximately 100% breakthrough of methyl iodide was measured in the first two segments.

The column material in all segments was examined and photographed. The other column was left intact and 2 volume % NO_2 in air was metered to it for 45 hours. The column was then removed, examined and photographed.

The material in the first two iodine saturated segments of the first column was pure yellow, the third segment was a mixture of yellow and black, and the last two segments were black. The yellow is characteristic of AgI and the black characteristic of silver oxide. The first 3 segments of the second column after metering NO_2 were pure white and the last two segments pure yellow. The first two segments of the second column were also saturated with methyl iodide prior to metering NO_2 and it was assumed that the corresponding segments of both columns looked the same before introducing the NO_2.

Further experimentation using NO_2 was scheduled including analysis of the materials in the columns to determine what was happening. Also scheduled was additional work with the demonstration unit using material A prior to work with a pilot plant size unit. However, the project was terminated at the end of fiscal year 1978.

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INTRODUCTION

Tributyl Phosphate $(C_4H_9O)_3\ PO_4$ diluted with dodecane (or normal paraffin hydrocarbon, NPH) is the solvent extractant commonly used in the PUREX process to separate uranium and plutonium from fission products in spent LWR fuel during the dissolution process. When recycled acid is used in the dissolution process, small amounts of NPH (normal paraffin hydrocarbon) the TBP vapor will be released to the off-gas streams, both from the dissolver and the vessel vent.

These gas streams will contain other airborne fission products released during the reprocessing steps which are required to be removed. Iodine and organic iodides are major radioactive constituents of these off-gas streams. Current proposed treatment methods for iodine removal involve the use of silver-loaded inorganic sorbents. European laboratory and pilot plant studies have shown that the presence of TBP vapor in the gas streams reduce the capacity of the silver beds to remove iodine resulting in more frequent replacement of the silver beds.[1] Studies at the Karlsruhe Reprocessing Pilot Plant (WAK) have shown that airborne TBP in concentrations of approximately 6 mg/ℓ significantly reduced the iodine sorption capacity of AC6120 material. Removal efficiency of AC6120, however, could be restored by introducing NO_2 into the air stream. Dodecane was found to have no deleterious effects.

Little work addressing this problem has been done in the United States. The presence of TBP/NPH in the off-gas streams has been recognized as a possibility since PUREX flow sheets were prepared and plants built at Hanford and Savannah River to reprocess spent military fuel. The addition of NO_2 to the off-gas streams to reduce the effect of TBP contamination may be a viable option for European plants using AC6120 material because of the unique chemical composition of AC6120. However, if future domestic plants use silver substituted zeolites (faujisite) or mordenites as iodine sorbents, this may not be feasible. Work with silver mordenites and silver zeolites has shown that the presence of NO_2 significantly reduces the loading of iodine.[2]

If dissolver and vessel off-gas treatment includes the use of silver zeolite or silver mordenite, TBP must be removed prior to iodine removal to assure efficient use of the silver. The approach taken in the research work described is to define treatment or removal methods for TBP which are compatible with downstream processes for removing iodine and demonstrate these removal methods.

GENERAL APPROACH

Processes to treat or remove TBP from off-gas streams have to meet certain requirements to be incorporated into fuel reprocessing flow sheets. The primary consideration was compatibility with proposed processes to treat off-gas, primarily the process to remove iodine. The TBP treatment process would need to be space efficient, relatively uncomplicated and amenable to remote handling and control.

After examining several options, a treatment method incorporating a solid inorganic sorbent was selected as a potential method. This type of treatment would be compatible with iodine treatment methods proposed. Handling and disposal methods for the waste generated from removing TBP could be identical to those used for iodine. Space requirements would be minimal and the design would be simplified for a dry removal process.

A literature survey was conducted to identify possible inorganic sorbents having properties indicating their effectiveness to remove TBP or similar organic compounds. The required material would have a surface area <500 m^2/g to minimize water sorption, a pore diameter greater than approximately 30 Å to accept a molecule the size of tributyl phosphate and be able to withstand temperatures up to 170°C. Sorbents showing an affinity to "fix" phosphates such as alumina or iron-containing materials were considered. Candidate materials selected for study included silica gels, alumina, acid treated clays and zeolite molecular sieves.

Before any laboratory work could begin, a sensitive quantitative analysis technique for measuring very low concentrations of TBP was to be developed. Gas chromatography was successful for analysis of liquid TBP

and the use of a gas chromatograph for direct vapor injections of airborne TBP was to be explored, along with other potential methods. However, a continuous real time analysis instrument was most desirable due to the nature of the planned experiments.

A series of laboratory and pilot plant experiments was developed. Initial screening studies in the laboratory using packed beds of small amounts of material in short term TBP loading experiments were designed to identify promising materials for future work. The candidate material would be used in parametric experiments using only TBP in an air stream to identify the most promising material for further laboratory experiments. Tests using variations in flow rate and TBP loading rate would be conducted. Final laboratory experiments would be conducted using a simulated reprocessing off-gas stream containing some constituents found in actual reprocessing streams.

The final phase of the study was to involve demonstrating the selected air cleaning system in the Nuclear Waste Vitrification pilot plant at Pacific Northwest Laboratories which can operate as a fuel reprocessing pilot plant. Part of this work was to measure the typical TBP vapor concentrations found in off-gas streams. The demonstrated TBP removal system was to be installed in an off-gas stream at an operating fuel reprocessing plant such as at Savannah River or Hanford to assess its effectiveness under actual operating conditions. Part of this task would also involve measuring TBP vapor concentrations at the full scale plant.

QUANTITATIVE ANALYSIS

TBP ANALYSIS

Laboratory work was initiated to develop a sensitive method to quantitatively analyze TBP vapor as low as 0.1 mg/m^3. The initial method explored was to trap TBP vapor on activated carbon impregnated filter papers (Schleicher and Schuell #508), and analyze for the phosphorus by X-ray fluorescence.

A series of standards of known mass of phosphorus from liquid TBP (99% pure) ranging from 2.3×10^{-5} to 1.1×10^{-2}g P were statically prepared on the charcoal filters. Sections of the filters were analyzed by X-ray flourescence. A phosphorus gradient on the filters from front to back was identified by the analyses. The amount of phosphorus detected was also inconsistent between the filter samples and among samples.

An attempt was made to dry macerate and homogenize the filter paper and press it into a suitable size for analysis to give a uniform phosphorus distribution. Aliquots (about one-half of the macerated filter) were pressed very thin for analysis. The sample preparation process was not found suitable for X-ray analyses and consequently the effort was terminated.

An analysis method for organic phosphate pesticides outlined in the National Institute of Occupational Safety and Health (NIOSH) procedures was explored for TBP vapor samples.[3-5] This method involved: 1) collecting TBP by sparging the TBP/air mixture through a known amount of ethylene glycol until at least 0.01 mg TBP was collected, 2) extracting TBP from the glycol into hexane, 3) reducing the hexane volume to 1 mℓ, and 4) injecting 2 μℓ aliquots of hexane/TBP into a gas chromatograph equipped with a flame ionization phosphorus detector.

The chromatograph column used in this analysis was 5.5 ft x 1/8 in. Pyrex packed with 5% QF-1 and 5% DC-11 on 80/100 Varaport 30. Column temperature was 185°C to 190°C, injection temperature 205°C to 210°C, and detector temperature 210°C to 215°C. These conditions gave a minimum detectable concentration of 0.0048 mg TBP/mℓ hexane (or 0.005μℓ TBP). The overall precision for the analytical portion of the procedures was ±25% equally distributed between the hexane extraction and the gas chromatograph analysis.

Laboratory experiments were conducted to test the ability to generate, manipulate, and measure very low concentrations of airborne TBP vapor using the NIOSH method. TBP was generated by bubbling dry nitrogen through liquid TBP in a temperature controlled gas wash bottle and feeding the mixture into a dilution air stream. The TBP laden air stream was then metered into known volumes of ethylene glycol through an impinger.

The TBP trapped in ethylene glycol was analyzed along with known prepared samples of TBP liquid in glycol as a check of the reproducibility of the analysis technique. Results indicated that the accuracy of the analysis was ±27% at a 95% confidence level for samples <10 mg TBP/50 mℓ ethylene glycol.

Turnaround time for analysis was longer than desired, however, and a modification in the procedure was instituted to improve the analysis time. A hexane cold trap was substituted for the ethylene glycol to collect the TBP. The hexane was cooled to 0°C with acetone-dry ice, and the airborne TBP vapor was sparged through the hexane. The hexane sample was concentrated and analyzed for TBP eliminating the extraction steps. Analysis performed on prepared samples indicated an analytical accuracy of ±10% at a 95% confidence level which was considerably better than the ±27% for analysis using the TBP extraction from ethylene glycol. However, this analysis was neither continuous nor real time and required several steps to obtain a result. (Note: The reproducibility of the overall method of TBP generation, sampling, and measurement was evaluated as part of the investigation of the efficiency of several candidate sorbents to remove TBP. Results of these studies are found in the subsection titled, Initial Screening Studies under the Experimental section.)

An alternative method was tried in which vapor samples were injected directly into a Hewlett Packard 5730 gas chromatograph, equipped with a N_2/P-flame ionization detector and associated integrator.[6] This method was an improvement over the NIOSH method because results were nearly instantaneous and closer to a real time analysis. Optimum analysis conditions for TBP as a vapor were established in the chromatograph during liquid analysis. However, direct vapor injection using gas-tight syringes was not found to be a viable analysis. The response to repetitive injections was not reproducible, even though the chromatograph readily detected the low concentrations of TBP used in the experiment. The TBP vapor appeared to be either reacting with the Teflon* tip in the syringe and/or being adsorbed on the stainless steel needle. Chromatograph response for very

* DuPont Trademark.

low concentrations of TBP in hexane (liquid injections) were found to be reproducible and confirmed that the problems associated with the vapor injection were due to the manipulation of the vapor and not to the ability of the chromatograph to analyze samples.

A continuous real time instrument for vapor phase phosphorus analyses was identified with the capability to detect phosphorus near 0.1 mg/m^3. The instrument, a Meloy Laboratories, Inc. PA460, performed real time and continuous, unattended dry analysis of phosphorus compounds in gas mixtures utilizing a unique flame photometric detector.

The instrument was found suitable for TBP vapor analysis after modifications. TBP was found to sorb onto and degrade the Teflon* tubing used in the internals of the instrument. The pathway the TBP followed to the detector was altered to pass only through specially treated chromatographic grade stainless steel tubing and special bellows valves.

The instrument was calibrated using a TBP vapor generation system described in the Experimental section of this report. Calibration was performed over several weeks to establish the best procedure to use and to determine which procedure would give a reproducible calibration curve.

Airborne TBP concentrations used for calibration were determined from vapor pressure data.[7] The calibration system allowed concentrations to vary over 3 orders of magnitude. The response of the instrument to a given calculated TBP concentration varied by only $\pm$15% (at the 95% confidence level) over a month's use. The instrument was capable of detecting TBP concentrates as low as 0.12 mg/m^3 and was used for the last two years of the experimental work.

METHYL IODIDE ANALYSIS

In the final phase of this study low concentrations of methyl iodide vapor were used. Quantitative analysis of methyl iodide was done with a Hewlett Packard 5730 gas chromatograph equipped with a Ni^{63} electron capture

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* Dupont Trademark.

detector. Output from the chromatograph was recorded on a Hewlett Packard 3380 reporting integrator.

The chromatograph was equipped with a 5% SE 30 column kept at 50°C. The injector and detector were both set at 150°C. Carrier gas was argon/10% methane flowing at 60 cc/min.

Calibration of the chromatograph was performed using the vapor above methyl iodide liquid in a sealed bottle. Methyl iodide vapor was assumed to be an ideal gas at atmospheric pressure and all calibration calculations were based on this assumption.[8,9] A very small vial partially filled with methyl iodide liquid and sealed with a septum was immersed in an ice bath at 0°C. A measured volume of this vapor was withdrawn with a gas-tight syringe and injected into sealed dilution flasks of known volume which were flushed with dry nitrogen. Depending on desired concentrations, samples of this dilution were either injected directly into the gas chromatograph or into a similar dilution flask. Samples from the second dilution flask were injected into the chromatograph. The minimum detectable concentration of methyl iodide was 1×10^{-3} mg/m^3 CH_3I.

By using various size syringe samples and taking samples from the dilution flasks, a complete calibration curve covering the entire mass range of methyl iodide encountered in the experiments were constructed. The accuracy of this method of calibration was estimated to be $\pm$4%. The major contributing errors were found in determining concentrations from vapor pressure data, measuring volumes of dilution flasks and syringe samples and temperature measurements.

The precision of the calibration over the several months duration of the experiments was about $\pm$10% at the 95% confidence level. Precision was enhanced by the use of 3380 recording integrator which automatically records peak areas and by the fact that the Ni^{63} detector was stable over a long time period.

LASER ANALYSIS

The possibility of using laser methodology as an in situ measurement technique for TBP in gas streams was explored. Some development work was

initiated by engineers at PNL who are laser experts. A preliminary feasibility study was conducted which concluded that selective laser analysis of the low concentration of TBP expected in off-gas streams was achievable using current state-of-the-art instrumentation.

A helium cooled optoacoustic laser was selected to use in experimentation. A special diode necessary for analysis was procured. Initial laboratory experiments to assess the effect of all potential interfering species were designed using a simulated gas stream. Equipment problems caused a delay of several weeks and eventually the funding was discontinued before laboratory experimentation could be initiated.

EXPERIMENTAL

INITIAL SCREENING STUDIES

Several commercially available sorbent materials identified through manufacturer's literature and known applications were obtained for use in the initial screening studies to evaluate TBP retention. The materials selected were either silicon oxide, aluminum oxide or combinations of magnesium, silicon, alumina and iron oxides. Two materials, activated charcoal and H, were used as a reference material for comparison with the other materials. These short studies were run at one set of conditions and were designed to identify sorbents showing a high TBP retention for use in further parametric long term loading experiments. Identification of the materials chosen is given in Appendix A.

The analysis method used in these studies was the one developed using the ethylene glycol trap with gas chromatographic analysis of the hexane/TBP extractant. Later, the method was altered to employ the hexane cold trap in place of the glycol. The apparatus for these experiments is shown in Figure 1.

Commercially available sorbents were packed 5 cm deep in a 2.5 cm diameter stainless steel column which was placed in an oven maintained at 100°C. The feed stream to the column consisted of TBP vapor in dry nitrogen

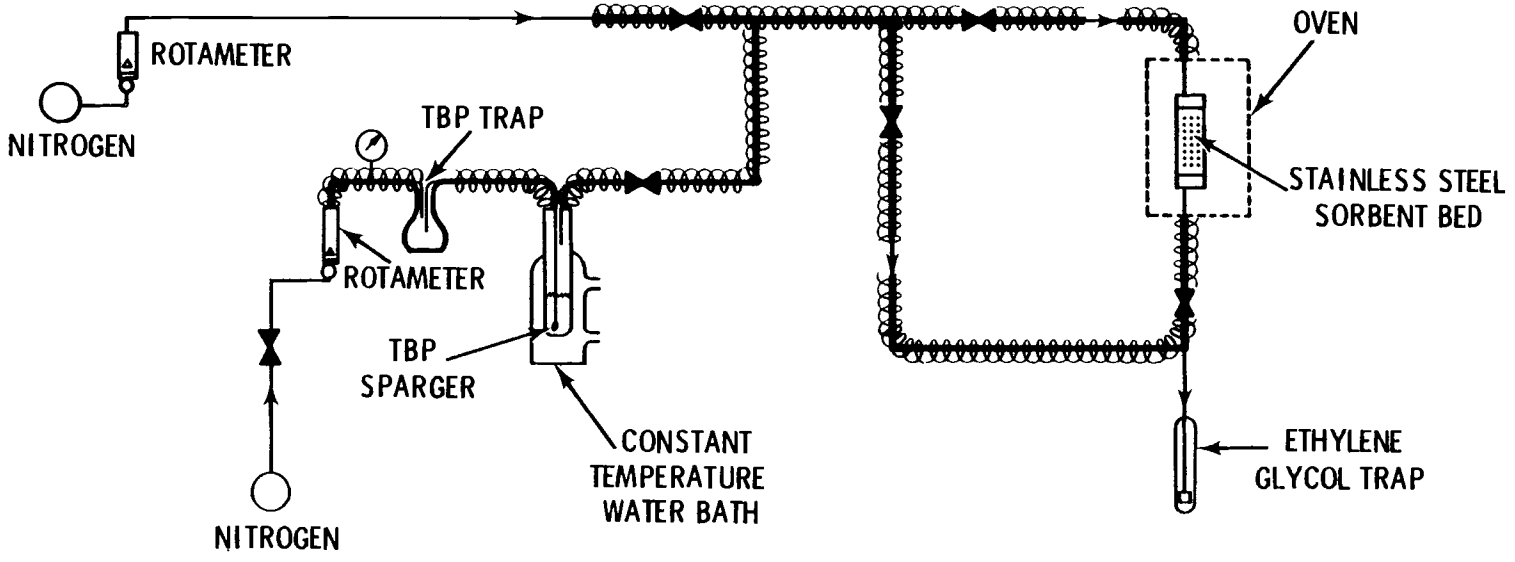

FIGURE 1. Schematic Diagram of Apparatus Used in Initial Screening Studies.

flowing at 172 mℓ/min. TBP vapor was generated by sparging nitrogen at 72 mℓ/min. through TBP liquid kept at a constant temperature greater than 80°C. A side stream of dry nitrogen flowing at 100 mℓ/min. was combined with the sparger stream to make up the feed stream. All feed lines in the system were stainless steel and heated where necessary to prevent condensation. Temperature and pressure were continuously monitored.

Prior to each experiment samples were taken of the bed inlet feed stream by sparging the total stream through ethylene glycol to establish the inlet TBP concentration. Measured TBP concentration ranged from 400 to 1000 mg/m^3. Experiments were started by diverting the feed stream to the bed. The effluent from the bed was passed through the glycol. Samples were taken in one hour increments continuously for a total of three hours. In several test runs a sample was also taken of the carrier gas (N_2) alone which was passed through the bed material for one hour at the end of the test to measure any TBP eluting from the bed. Each ethylene glycol sample was analyzed for TBP. Efficiency of the material to remove TBP was determined by calculating the retained percentage of the total TBP metered to the bed. Table I is a summary of the results. The amount of material used in each experiment is given in Appendix B.

In all materials except material G, retention efficiency appeared to improve after the first hour of run time. The amount of TBP in the samples for the second and third hours decreased or remained the same. This apparent anomaly is consistent among the materials. One theory is that the bed material needs to be conditioned with TBP for a period of time before becoming an efficient trap. Further experimental work would be required to establish how long the trend would continue. In no instance was any significant amount of TBP found to elute from the material at the end of the loading experiment.

From Table I it was concluded that the most efficient materials (∿95% TBP retention) were A, D, H, K, and L. Material H was not considered a candidate material, however, since it contained charcoal plus other unknown chemical species in a mixture. None of the materials, except material G, retained less than ∿90% of the metered TBP.

TABLE I

Tributyl Phosphate Removal by Sorbents, Airflow 172 cc/min.
Bed Temperature 100°C, Bed 5 cm Deep x 2.5 cm Diameter

Material	Inlet TBP, mg	Outlet TBP 1st hr, mg	2nd hr, mg	3rd hr, mg	Total, mg	TBP in N_2 for 1 hr Flush Following Run, mg	% TBP Retention
Charcoal[a]	1.8	0.119	0.031	0.005	0.155	0.008	91.4
A	1.8	<0.005	<0.005	<0.005	<0.015	<0.005	>99
	2.6	--	--	--	0.22[b]	--	91.5
B	1.9	0.14	0.008	0.808	0.156	0.008	91.8
C	1.4	0.071	(c)	0.008	--	0.008	--
D	1.5	0.015	<0.005	<0.005	<0.025	<0.005	>98.3
E	2.6	0.14	0.01	<0.005	<0.155	<0.005	>94
F	2.0	0.16	0.064	<0.005	<0.229	0.005	>89
G	1.9	0.34	0.039	0.20	0.579	0.005	70
H	1.6	0.006	<0.005	<0.005	<0.016	<0.005	>99
J	2.4	0.16	0.038	0.019	0.217	0.006	91
K	19.8	0.67	0.069	0.041	0.77	--	96.1
L	19.8	0.37	0.061	0.029	0.47	--	97.7
M	9.6	0.52	0.099	0.035	0.654	0.018	93.2

(a) Coconut base
(b) Total of 4.5 hr run time
(c) Sample lost

The specified inlet concentration of TBP in this series of experiments extending over a period of about four months had a standard deviation of 25% at the 95% confidence level. Each screening test, however, was performed over a relatively short time period during which more nearly constant conditions could be monitored; thus, the individual bed removal efficiencies (% TBP retention) were more accurate than represented by the standard deviation determined over the full range of these experiments.

The most promising sorbents, A, D, and L, were chosen for further experimentation. The next series of experiments was conducted to assess TBP retention of these materials at operating conditions more nearly approaching those likely to be found in actual reprocessing off-gas streams.

PARAMETRIC STUDIES

These experiments were designed to evaluate the sorbent materials under various operating conditions of flow and TBP concentration. The best material as determined early in these experiments was used in experiments in later laboratory studies using a simulated process stream. The apparatus used in these experiments is shown in Figure 2. The apparatus (minus the column) was also used for calibration of the Meloy Laboratories, Inc., PA460 continuous phosphorus analyzer used throughout these studies. This instrument was not available for the earlier screening studies.

TBP vapor for parametric experimentation was generated by sparging cylinder air at a low flow through two temperature controlled gas washing bottles in series. The first bottle was at 96°C and the second at 60°C. Vapor pressure data indicated a saturated air stream. The TBP vapor concentration was reproducible. This configuration was necessary due to the low TBP vapor pressure (1 mm Hg at 100°C). The TBP vapor stream was mixed with cylinder air which was passed through a dry gas meter. The flows were regulated by rotameters to obtain the desired airborne TBP fed concentration.

After it was mixed, the feed stream flowed through 6 mm glass tubing to the bed of the material which was packed in glass column segments. The selected materials from the screening studies to be loaded with TBP were packed in the 2.5 cm diameter glass column shown in Figure 3. Approximately 3.8 cm of material was held in place by Gelman Type G glass fiber filters placed in front of stainless steel screens and snap rings to retain any fines purged from the material. A 6.3 mm sample port located just downstream of the material was used to sample the airstream leaving the bed segment. Airflow was upward through the system. As many as three column segments of material could be loaded with TBP during an experiment.

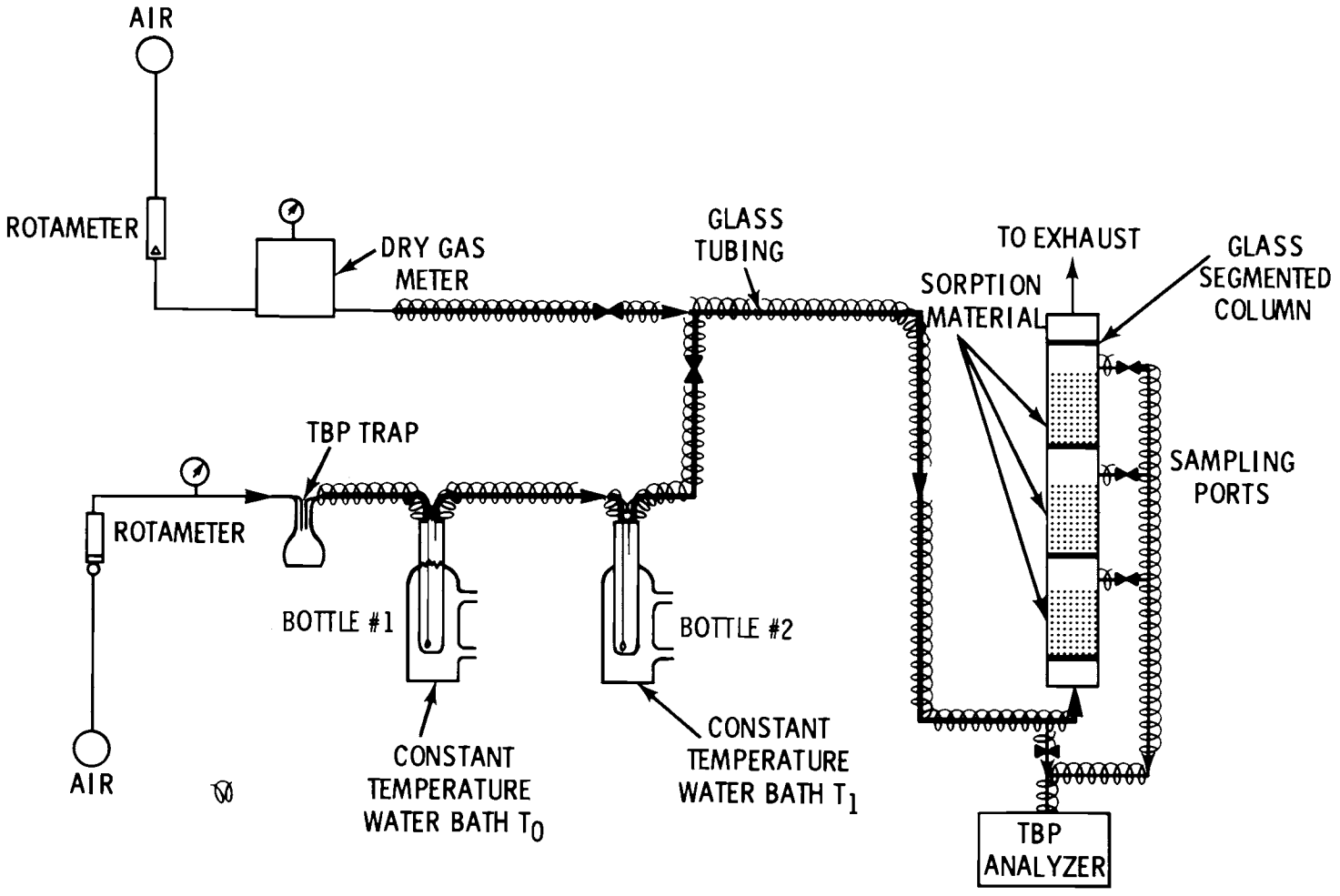

FIGURE 2. Schematic Diagram of Apparatus Used in Parametric Experiments Using Selected Sorbent Materials.

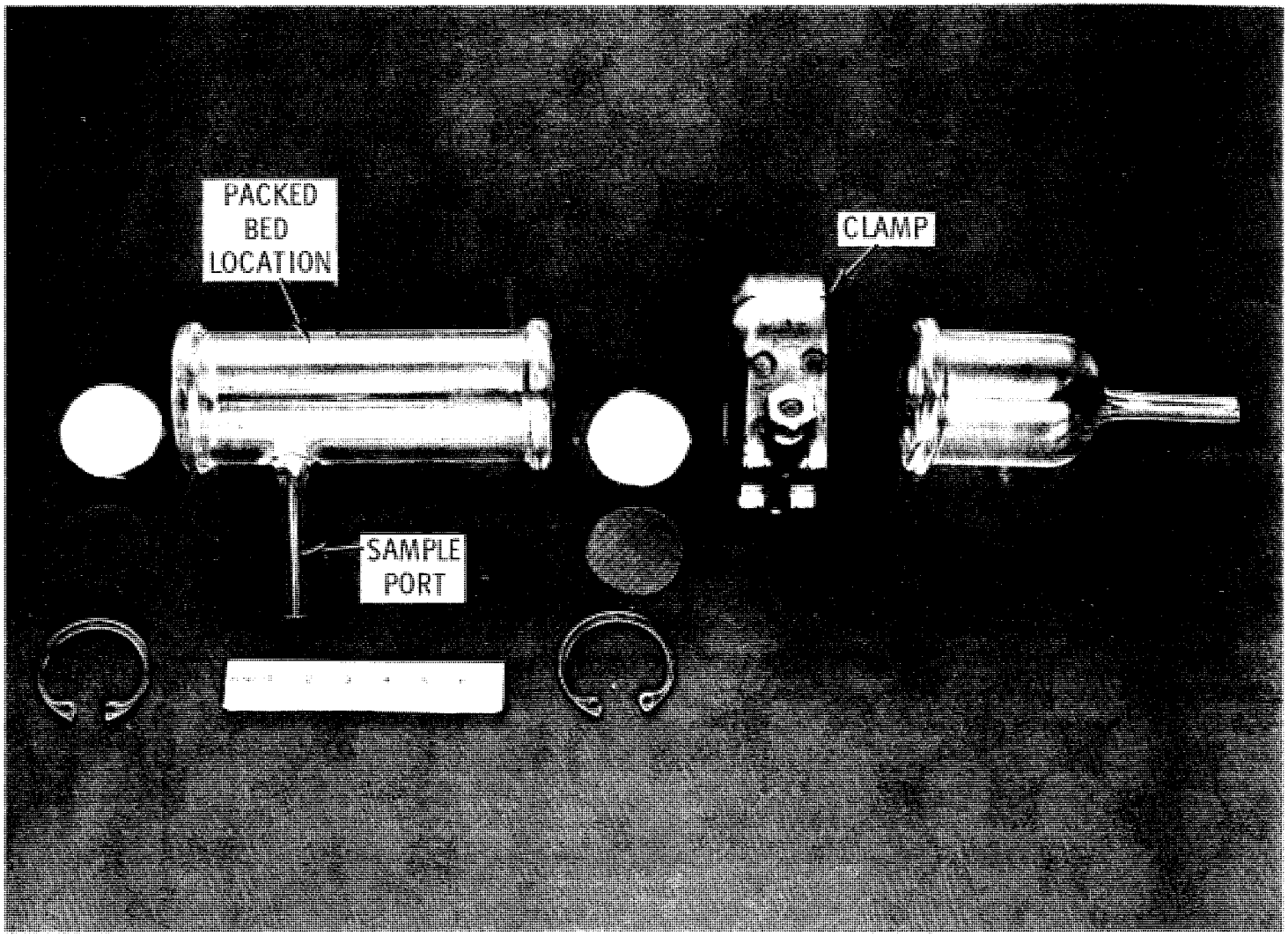

FIGURE 3. Glass Column Arrangement for Holding Material in Parametric Studies.

During an experimental run airborne TBP entering the inlet to the column was sampled via the sampling line to the PA460 analyzer. The PA460 draws a portion of the total feed stream at 200 cc/min. into the instrument. This inlet concentration (C_o) was sampled periodically. Samples of the airstream leaving each column segment were taken continuously to measure TBP concentration (C) breaking through the material.

Sampling concentrated on the first column segment until significant breakthrough was measured. Subsequent samples were taken of each column segment as necessary to follow breakthrough progression through the entire column. A ratio of C/C_o was calculated as a measure of breakthrough.

The calculated standard deviation in breakthrough calculations in this series of experiments was $\pm$25% at the 95% confidence level. The largest contributing errors in these calculations occurred in instrument calibration of the analysis of the inlet and outlet stream during experimentation.

Experiments with Material A

From the initial screening studies sorbent A, an 8 x 14 mesh granular activated alumina material, had the highest retention (first run) of the noncarbonaceous materials tested (Material H contained an activated charcoal mix), and was selected for further parametric study. Three column segments, containing 20 g of material A in each segment, were loaded with airborne TBP. The following conditions were employed.

Bed Temperature:	100°C
Average Airflow:	0.45 ℓ/min.
TBP Concentration:	100 to 240 mg/m^3
Preconditioning With Air:	2.5 hr

After more than 277 hours of run time and 1.8 grams TBP metered to the columns, a breakthrough of C/C_o = 0.02% in the first column segment was measured. No breakthrough in the other two column segments was detected. The concentration of TBP entering the columns was increased

during the test run from 100 gm/m^3 to 240 mg/m^3 to accelerate loading and breakthrough.

A second experiment using material A was prepared. A single column segment was packed with 19.1 g of material and loaded with TBP. Airflow was increased by a factor of 4 to assess the effect of this parameter. The following conditions were employed.

Bed Temperature:	100°C
Average Airflow:	1.9 ℓ/m
TBP Concentration:	100 to 450 mg/m^3
Preconditioning With Air:	2 hr

The material was loaded with 2.9 g TBP before any breakthrough (>0.01%) was measured. A total of 8.96 g TBP was metered to the material over a period of 331.6 hours before the run was terminated. Breakthrough measured at the end of the run was approximately 100%. The complete breakthrough curve is shown in Figure 4. Increasing the air flow by a factor of 4 resulted in 1.7 times more TBP retained per gram of material before detectable breakthrough.

The capacity of the material to retain TBP was calculated from the breakthrough curve to be 377 mg TBP/g material. Because of the high TBP retention of material A in these experiments, it was decided to use the material in future laboratory experiments run under simulated off-gas stream conditions. These experiments are described in the next subsection of the report, Bench Scale Demonstration Studies.

Experiments with Material D

TBP loading of 4 x 8 mesh spherical catalyst material D was initiated in late February 1978. A single column segment of material weighing 14.6 g was used in this first experiment. The following conditions were employed.

Bed Temperature:	100°C
Average Airflow:	1.9 ℓ/min.
TBP Concentration:	1000 mg/m^3
Preconditioning with Air:	2 hr

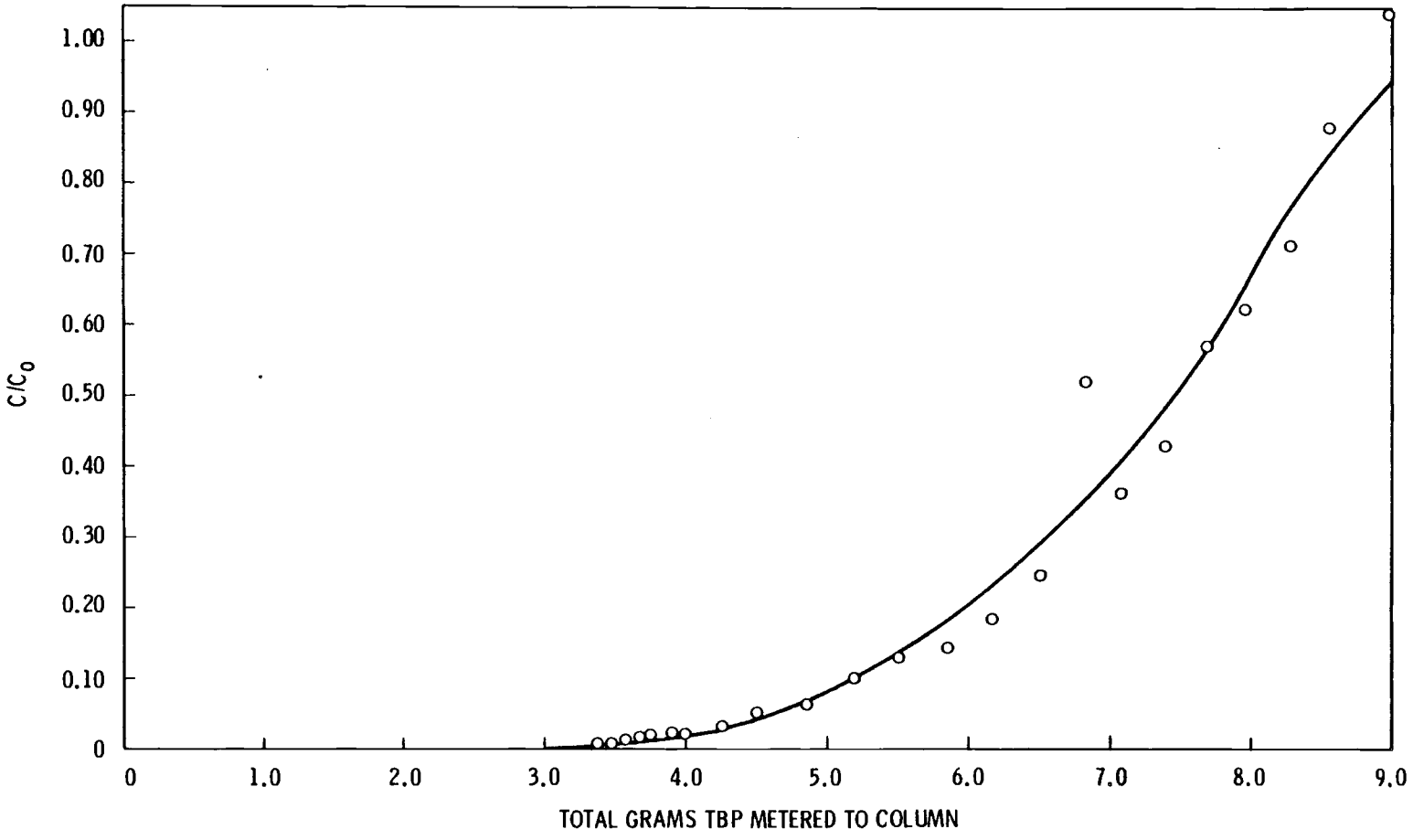

FIGURE 4. Breakthrough History for TBP Loading of Material A. Airflow 1.9 ℓ/min. Bed Temperature 100°C, TBP Concentration 100 to 450 mg/m^3.

Nearly instantaneous breakthrough was measured at the start of the experiment and 100% breakthrough was achieved after 37.6 hours of run time and 0.45 g TBP loaded onto the material. From the breakthrough curve in Figure 5, the capacity of the spherical material to retain TBP was calculated to be 11 mg TBP/g material, which was considerably less than the granular material A tested under nearly identical conditions.

This spherical material was crushed in the laboratory and sieved to 6 x 14 mesh in an effort to increase the surface area for reaction. The crushed material weighing 15.1 g was packed into a single glass column and TBP was loaded onto the material under identical conditions as those used for the spherical form of the material.

As in the experiment using the spherical form of material D, nearly instantaneous breakthrough was measured. The run was terminated after metering 0.97 g TBP to the material in 73.1 hours. The breakthrough curve for this material is shown in Figure 6. Calculated TBP retention of the crushed material was 39 mg TBP/g material.

Even though TBP retention was increased by 3.5 in the crushed form of material D, retention was significantly lower than achieved with material A. Further experimentation with material D was not considered.

Experiments With Material L

The next material used in these experiments was sorbent L, an 8 x 30 mesh granular, silica, alumina, magnesia sorptive clay, which indicated the third highest TBP retention of the noncarbonaceous materials in the screening studies. Two 3.8 cm x 2.5 cm glass column segments were packed with material L and prepared for loading with TBP. Segment 1 contained 13.6 g and segment 2 contained 14.0 g. The following conditions were employed.

Bed Temperature:	100°C
Average Airflow:	2.0 ℓ/min.
TBP Concentration:	60 mg/m^3
Preconditioning With Air:	2 hr

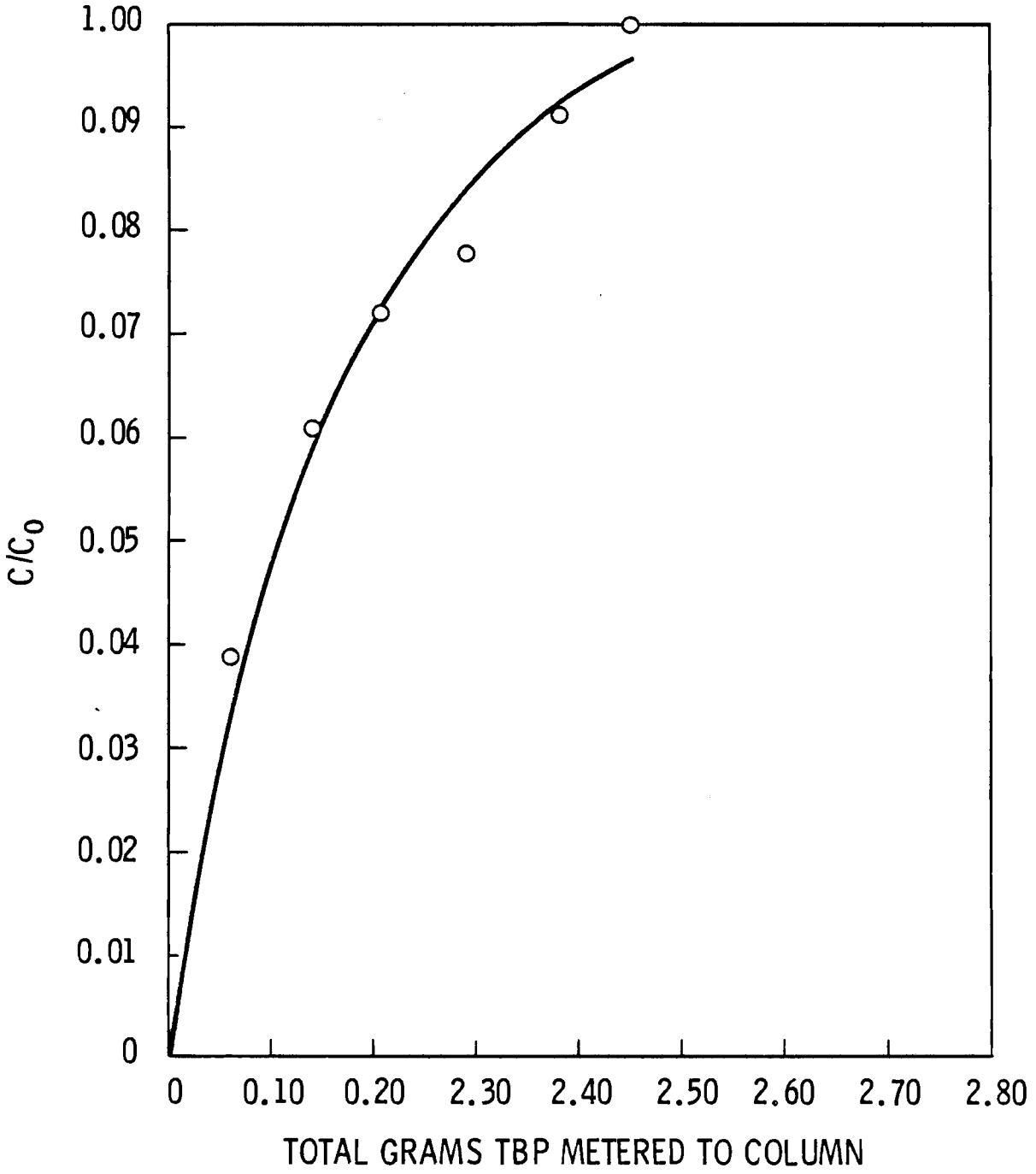

FIGURE 5. Breakthrough History for TBP Loading onto Material D (4 x 8 Mesh Spherical). Bed Temperature 100°C, Airflow 1.9 ℓ/min. TBP Concentration 100 mg/m3.

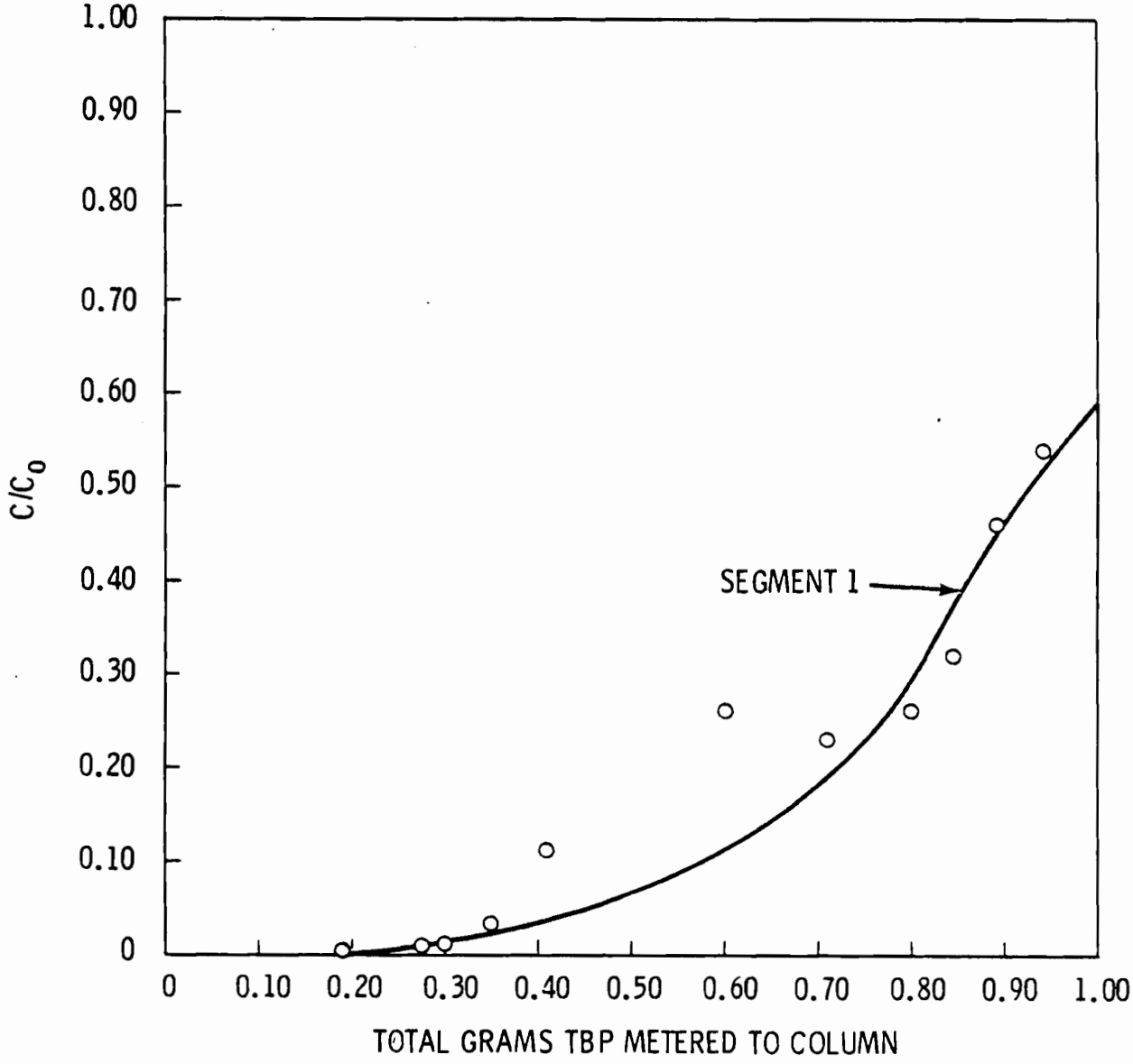

FIGURE 6. Breakthrough History for TBP Loading Onto Material D, (Crushed 6 x 14 Mesh). Bed Temperature 100°C Airflow 1.9 ℓ/min. TBP Concentration 100 mg/m^3.

A breakthrough of 0.6% in segment 1 was measured after metering 0.19 g TBP to the column. After metering 0.94 g of TBP to the material, a breakthrough of 54% was measured in the first column segment at which time the run was terminated. No breakthrough was measured in the second column segment. The breakthrough curve constructed for the first column segment is found in Figure 7.

Even though breakthrough was not followed to 100%, total capacity of the material can be estimated from the available breakthrough data. Approximate capacity of the material extrapolated to 100% breakthrough is 70 mg/g material which is greater than material D but considerably less than material A.

The initial screening studies were terminated in May 1978. Material A demonstrated the greatest TBP retention capacity of the materials studied and was selected for further laboratory experimentation to demonstrate the effectiveness of the material to remove TBP vapor and protect iodine sorbent material downstream. The experiments were conducted starting in April 1978 and are described in the next subsection.

Bench Scale Demonstration Studies

A bench scale demonstration unit was constructed to evaluate the effectiveness of selected sorbents to remove TBP under conditions approaching those in actual reprocessing off-gas streams. A feed stream of airborne TBP/NPH vapor, water vapor and methyl iodide was metered to packed columns of TBP sorbent and iodine sorbent. The measure of the materials' effectiveness for TBP removal was determined by the iodine retention of iodine sorbent material.

The experiments were conducted using the apparatus shown in Figure 8. The materials to be used were packed in two 2.5 cm diameter stainless steel columns. The column segments were held together by gaskets and snap joint couplings. A column segment is shown in Figure 9. The entire column assemblies were placed in an oven and maintained at 130 to 135°C for all experiments.

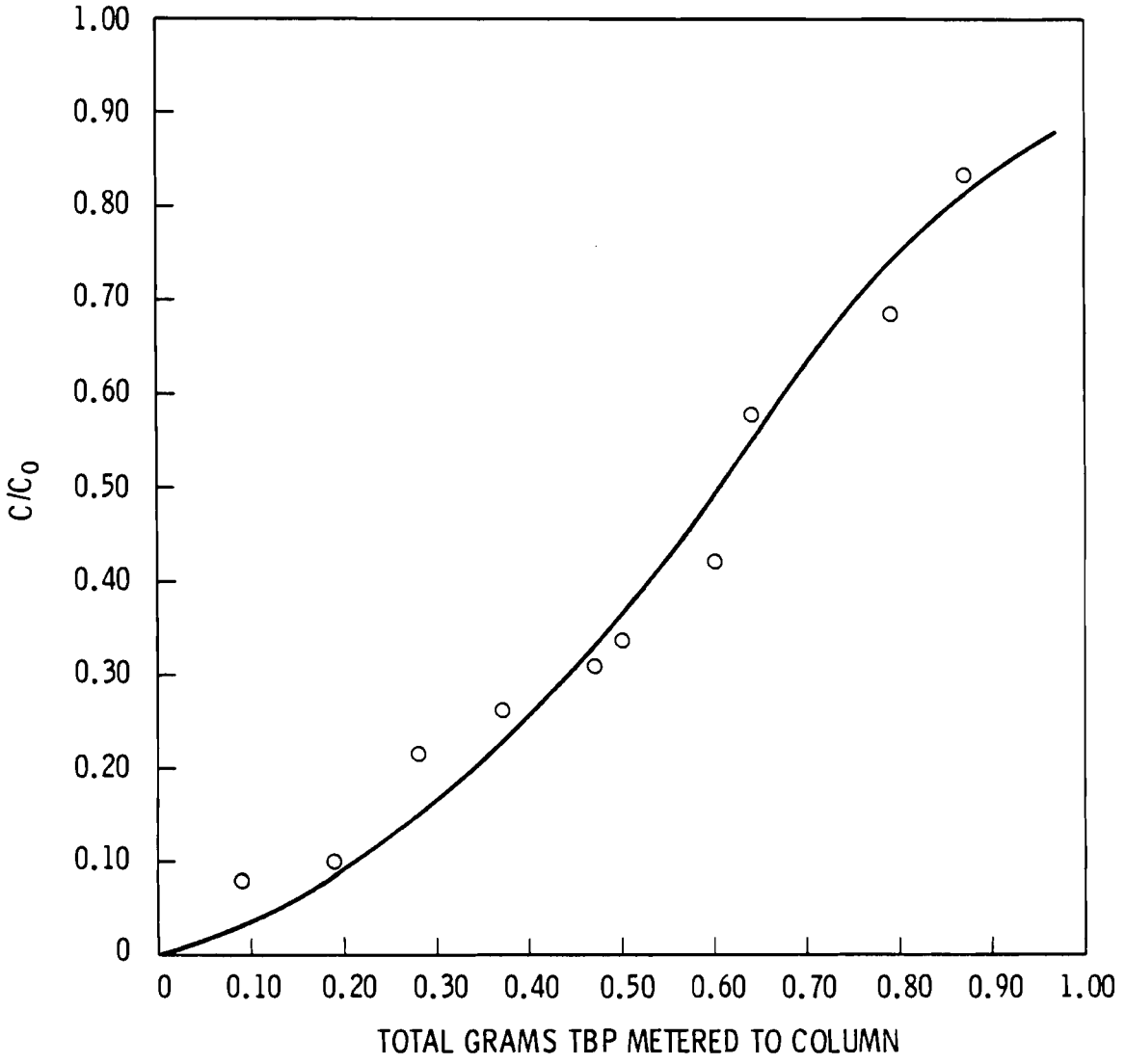

FIGURE 7. Breakthrough History for TBP Loading Onto Material L, Bed Temperature 100°C Airflow 2.0 ℓ/min. TBP Concentration 60 mg/m^3.

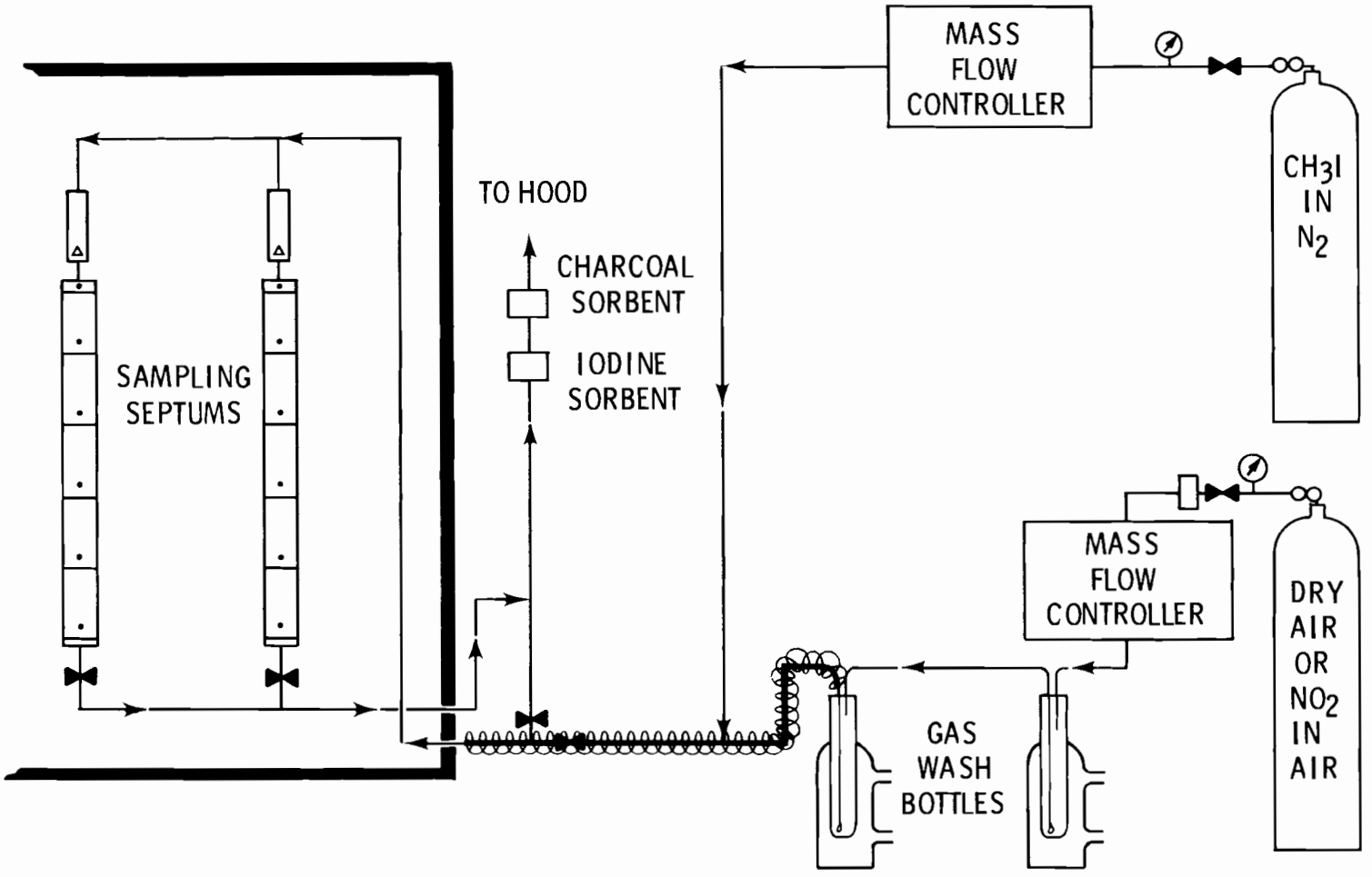

FIGURE 8. Schematic Diagram of Apparatus for Loading Iodine onto Selected Sorbents.

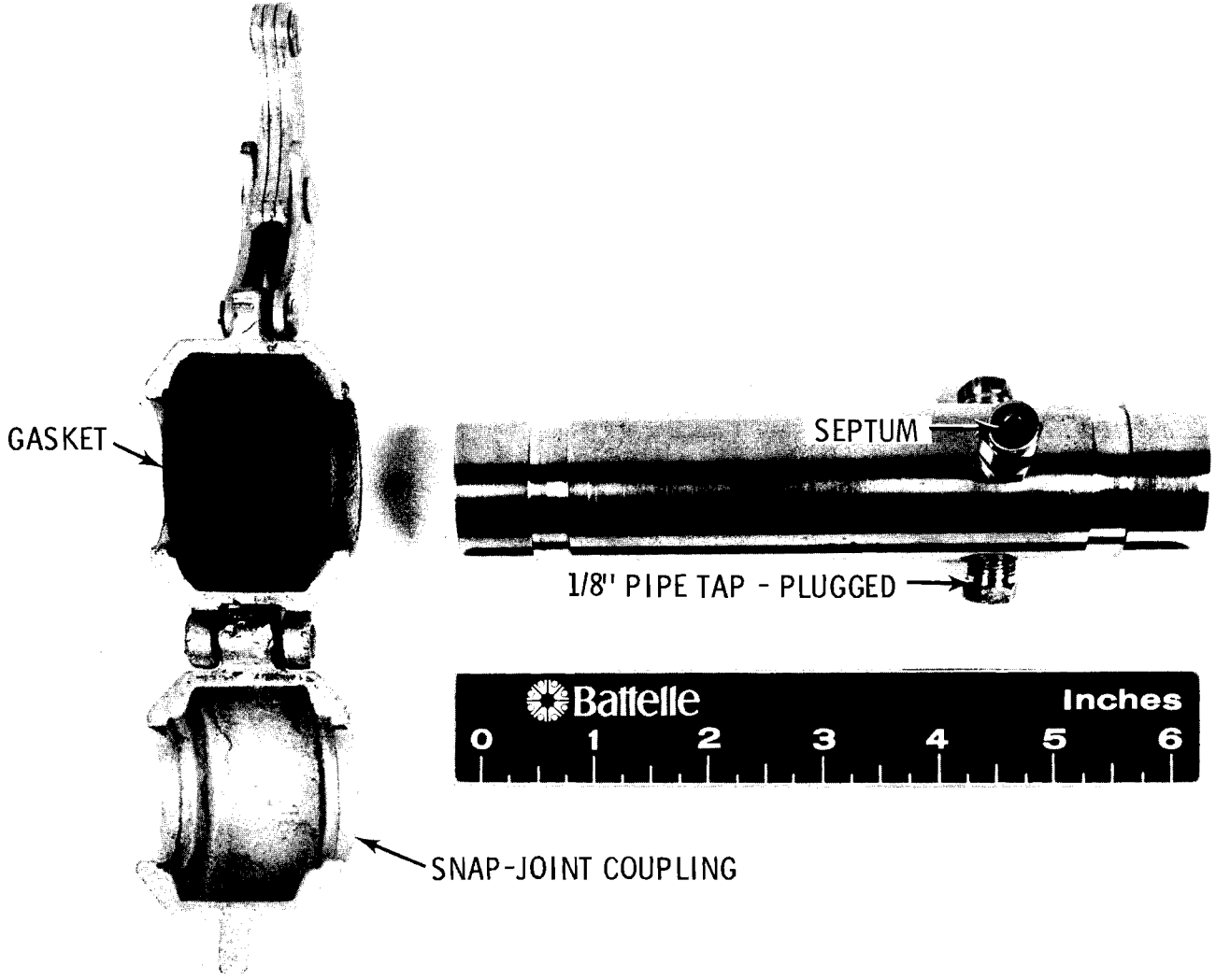

FIGURE 9. Typical Stainless Steel Column Segment for Retaining Sorbent Materials.

During experimentation, dry cylinder air was fed to two jacketed gas washing bottles maintained at 50°C by water circulated around the reservoirs. The bottles each contained a mixture of water plus 30% TBP in NPH. The stainless steel lines leaving the bottles were heated to 100°C. Methyl iodide vapor in N_2 was fed to the air stream by a Matheson mass flow controller and the entire stream was metered to the two columns through Matheson rotameters. Provisions were made to feed other vapors or gases into the main feed stream.

In preparing for an experiment, one segmented column would be packed with a commercially available iodine sorbent, the other column contained two sections of the selected TBP sorbent meterial followed by two or three segments of the same iodine sorbent as in the other column. The amount of material used in each experiment is given in Appendix C.

During an experiment, the air stream containing the TBP/dodecane, water vapor and known concentrations of methyl iodide would be metered to the columns. The breakthrough of methyl iodide measured by gas chromatography, was followed in each column segment throughout both columns. Methyl iodide analysis was performed by periodically sampling the feed streams to the columns and downstream of each packed bed segment with a gas-tight syringe through septum sealed sampling ports. Several experiments were conducted and the results are described.

An experiment was completed in late April 1978 using the bench scale demonstration unit to evaluate material A as a sorbent to remove TBP and protect iodine sorbent beds. Two 2.5 cm diameter stainless steel columns were prepared. Column I contained five 5 cm segments of a 7% Ag impregnated silica gel iodine sorbent and Column II contained two 5 cm segments of material A followed by three 5 cm segments of the 7% Ag impregnated silica gel iodine sorbent. The columns were preconditioned with air at 2% relative humidity for 20 hours and air and TBP/NPH vapor for 1.5 hours prior to metering methyl iodide.

Conditions for this experiment were air flowing at 1.9 ℓ/min. to each column and average methyl iodide concentration of 160 mg/m^3. The airborne TBP concentration was estimated at ∿800 mg/m^3 by measuring the volume loss of the 30% TBP/NPH liquid at the termination of the experiment.

At the end of the experiment 8.5 g of methyl iodide had been metered to each column. During the experiment, the breakthrough progression of methyl iodide through each segment of the iodine sorbent was followed. This breakthrough is represented as a graph of C/C_o versus grams methyl iodide metered with C = concentration of methyl iodide leaving a 5 cm column segment of sorbent and C_o = concentration of methyl iodide in the feed stream to the column. The breakthrough curves for Column I are given in Figure 10 and Column II are given in Figure 11.

To determine the effectiveness of the TBP sorbent to protect the iodine sorbent, a comparison of breakthrough curves was made between section A in Column I and section C in Column II, section B in Column I and section D in Column II and section C in Column I and section E in Column II. Table II is a summary of the breakthrough data.

The iodine retention of the iodine sorbent in section A and B of Column I and sections C and D of Column II was nearly the same. This indicated that material A contained in sections A and B of column II had little effect on the iodine retention of the iodine sorbent located downstream. More importantly, however, the data also indicated that iodine retention was near the stoichiometric maximum (within the uncertainty) and therefore the presence of the generated airborne TBP did not have a deleterious effect on the iodine sorbent.

It should also be noted that a small amount of iodine was retained by the TBP sorbent in sections A and B of Column II. This was unexpected and is assumed to be adsorption of the iodine onto the material. This same phenomena was noted in other experiments described below and the significance of the adsorption is discussed later in the report.

A second similar experiment was conducted. In this experiment, Column I contained two 5 cm segments of material A followed by three 5 cm

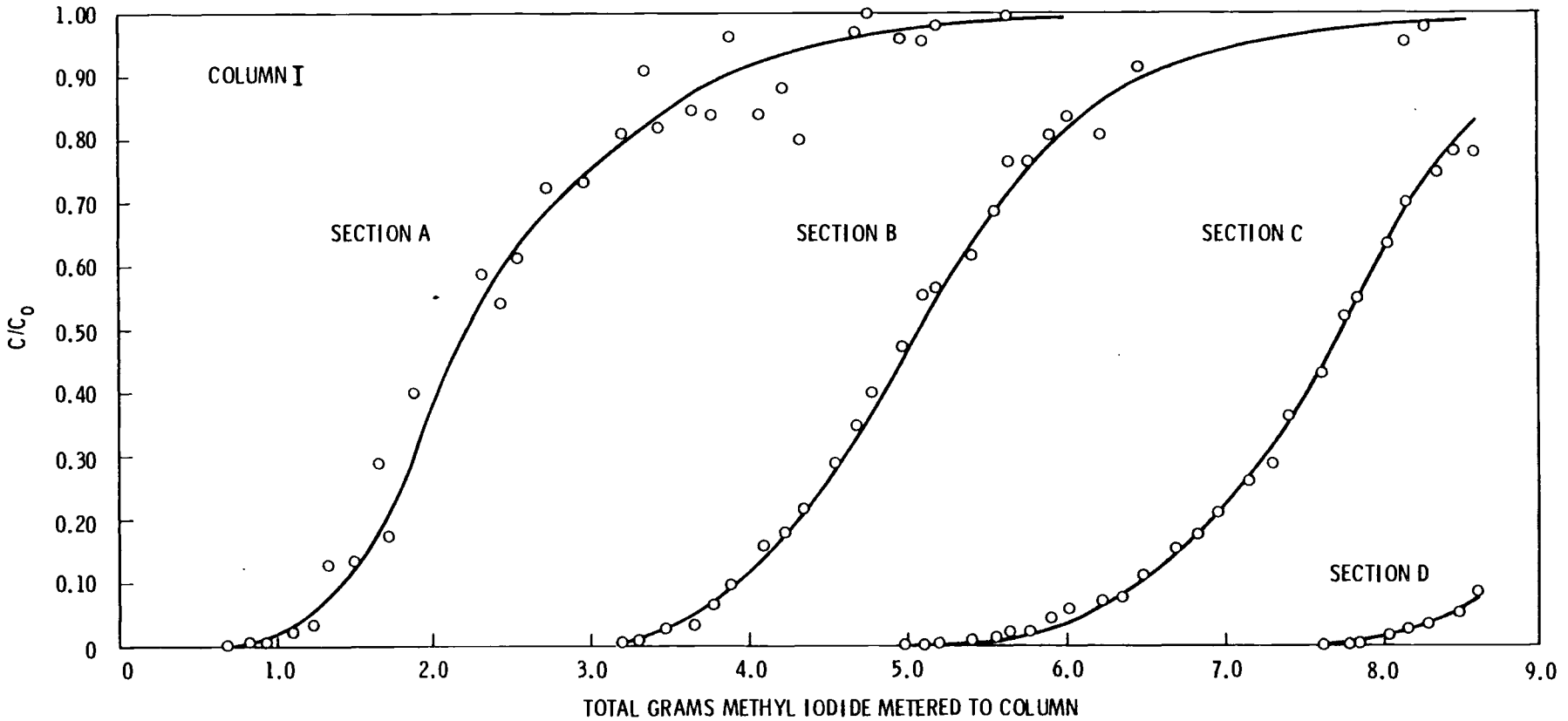

FIGURE 10. Breakthrough History for Methyl Iodide Loading onto 7 wt% AgI Impregnated Silica Gel Sorbent, Column I.

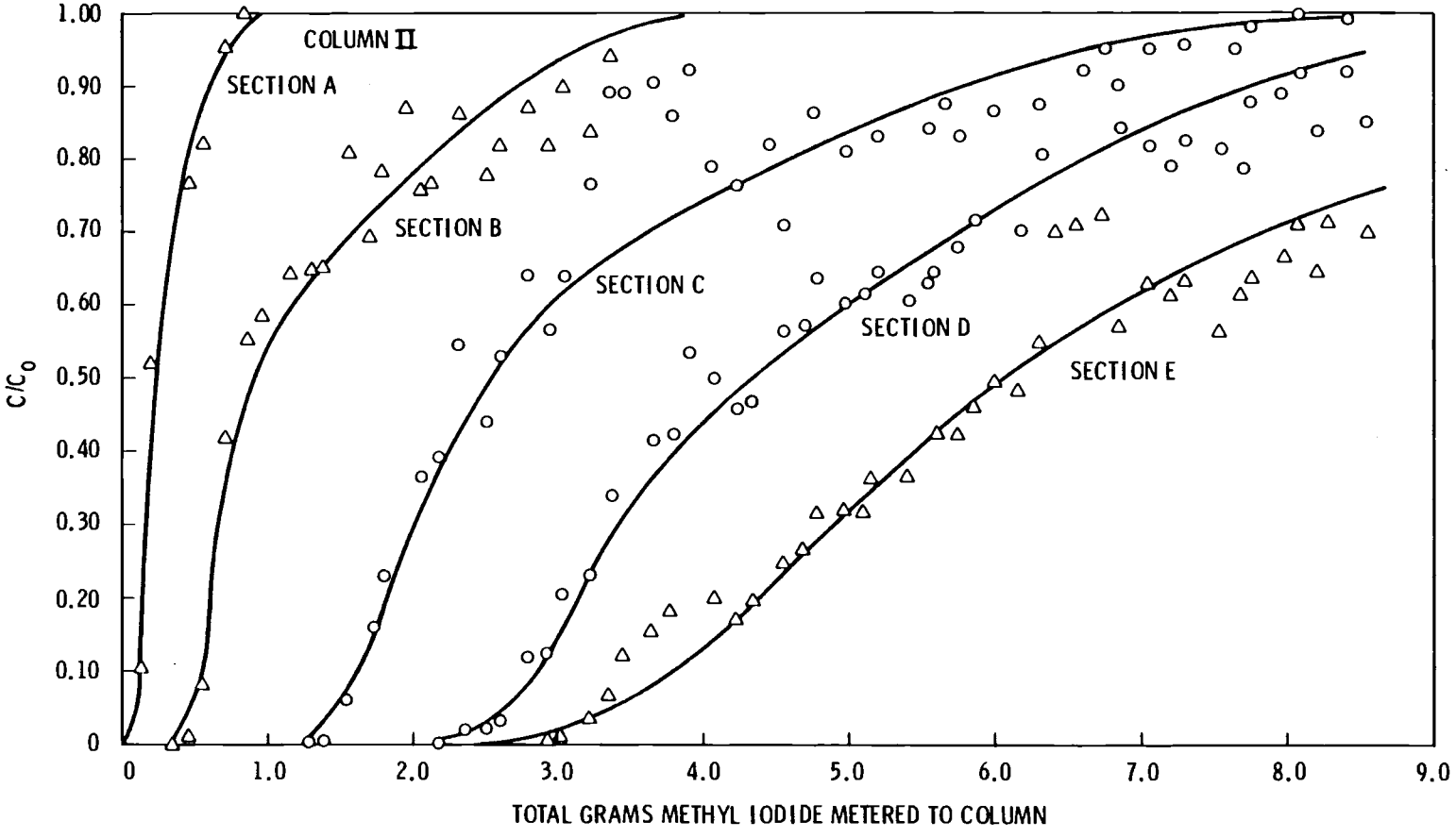

FIGURE 11. Breakthrough History for Methyl Iodide Loading onto Column II.

TABLE II

Analysis of Iodine Retention of 7% Ag Impregnated Iodine Sorbent

Sample	Measured % CH_3I Breakthrough (C/C_o x 100)	Calculated CH_3I Retention From Breakthrough Curves[a] gI/g Ag[c]	Theoretical Maximum[b] gI/g Ag
Column I			1.2
Section A	100	1.5	
Section B	98	1.4	
Section C	83	1.3	
Section D	7	0.9	
Column II			1.2
Section A	100 (material H)	(<.3)[d]	
Section B	100 (material H)	(<.5)	
Section C	100	1.5	
Section D	95	0.97	
Section E	76	0.77	

(a) Uncertainty is ± 25% at the 95% confidence level.

(b) Based on the reaction Ag + I → AgI.

(c) Based on 7 wt% Ag.

(d) Grams of Iodine.

segments of a 14 wt% Ag impregnated silica gel iodine sorbent. Column II contained five 5 cm segments of the 14 wt% Ag sorbent.

The columns were preconditioned with air at ∿2% relative humidity for 24 hours and air plus TBP/NPH vapor for 1.5 hours prior to metering the methyl iodide. During the experiment average airflow was 1.8 ℓ/min. and average methyl iodide concentration was 210 mg/m^3. Column temperature was 130 to 135°C.

Breakthrough of methyl iodide was followed until a total of 9.5 g was metered to Column I and 9.7 g to Column II. Methyl iodide was retained by Material A (Column I, sections A and B) as in the first experiment. Figure 12 is the breakthrough curves for Column I and Figure 13 is the breakthrough curves for Column II, sections A and B. No breakthrough was noted in sections C, D, and E of Column II.

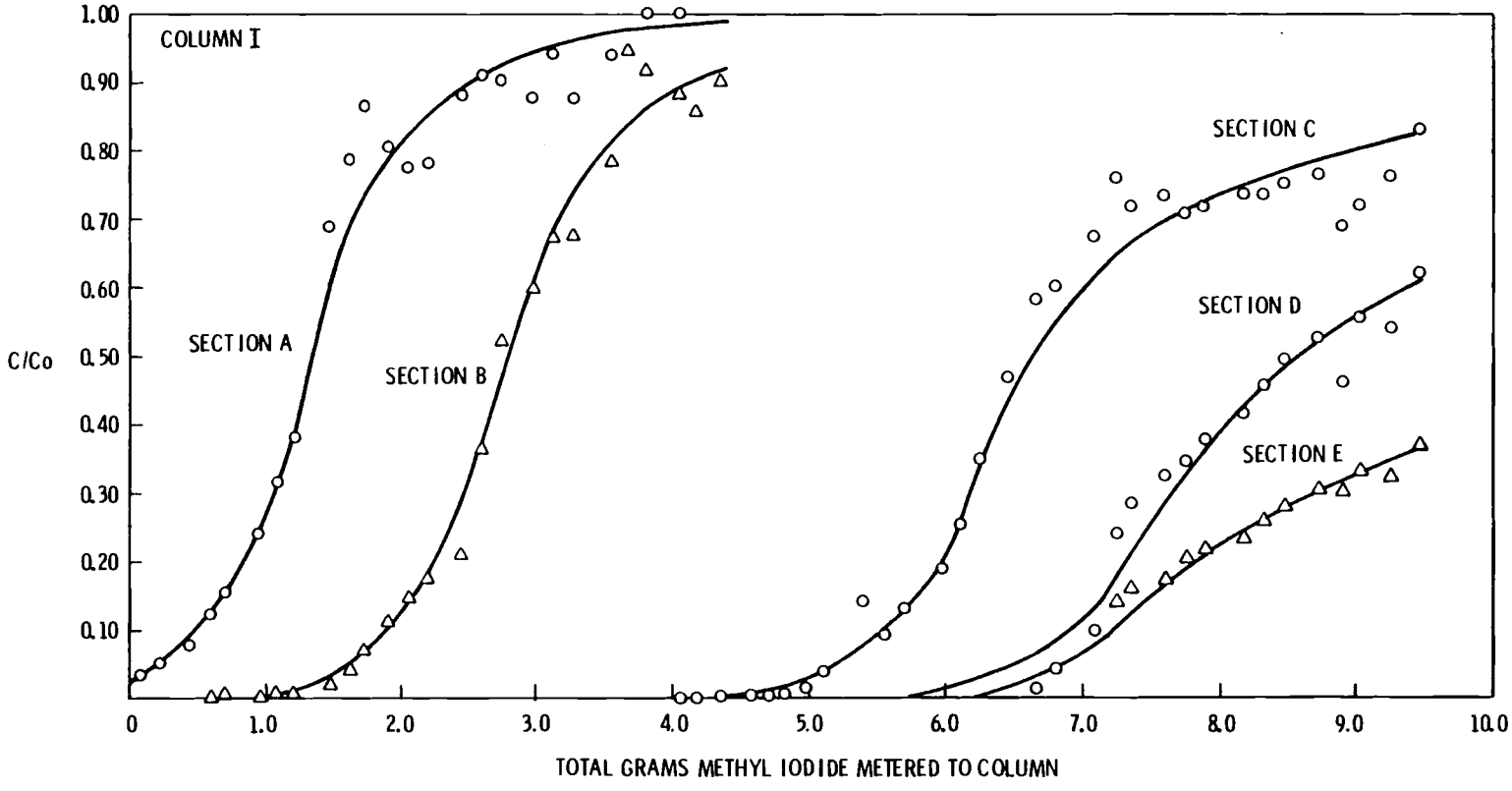

FIGURE 12. Breakthrough History for Methyl Iodide Loading onto Column I.

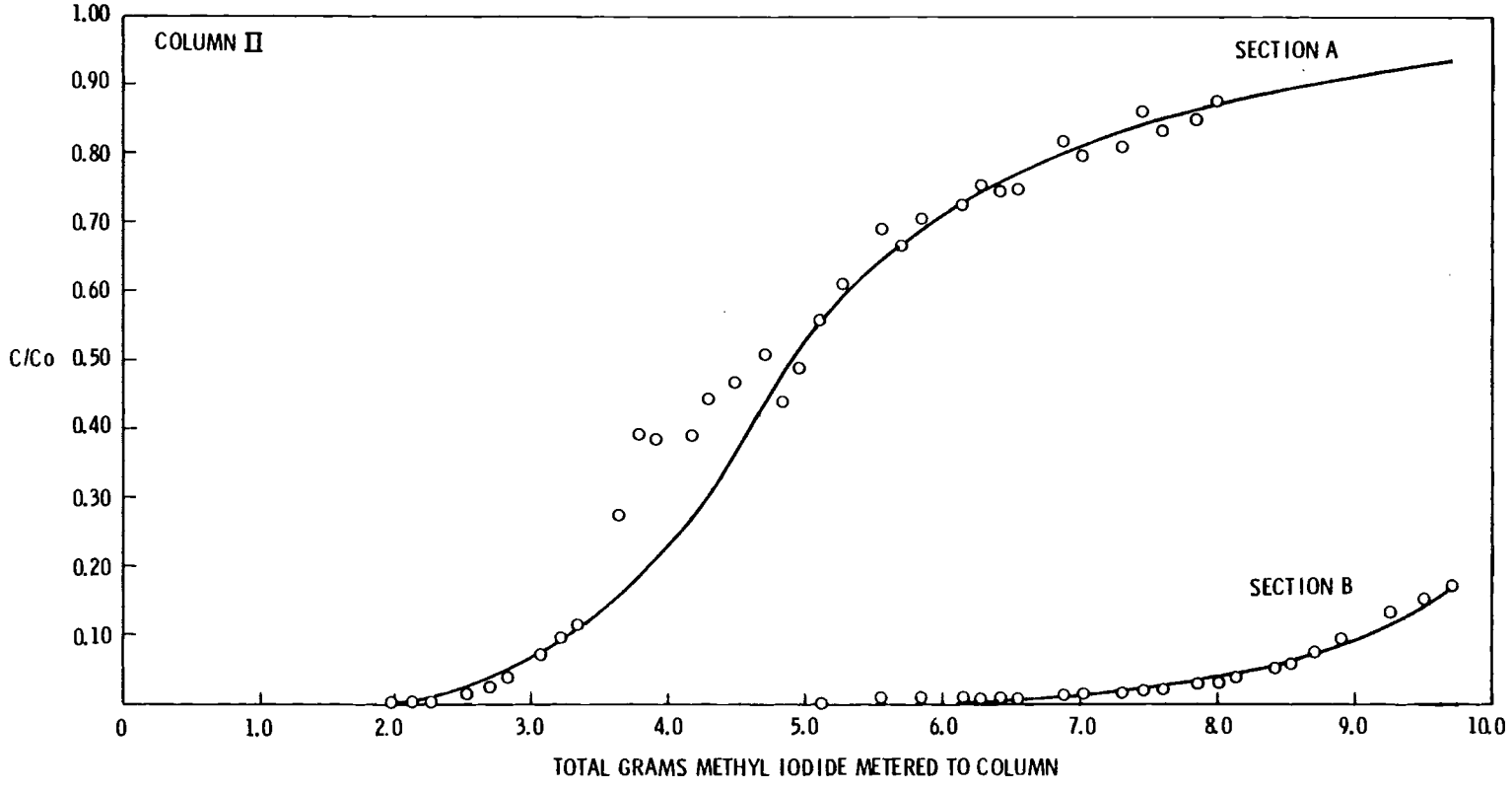

FIGURE 13. Breakthrough History for Methyl Iodide Loading onto 14 wt% Ag Impregnated Silica Gel Sorbent, Column II.

To determine the effectiveness of the TBP sorbent to protect the iodine sorbent, a comparison of breakthrough data is made between section C in Column I and section A in Column II, and section D in Column I and section B in Column II. Table III is a summary of breakthrough data.

The iodine retention extrapolated to 93% breakthrough in section C of Column I and section A of Column II was nearly the same within expected error. This indicated that the presence of material A in Column I had little effect on the iodine retention of this iodine sorbent. This was further confirmed by comparing the iodine retained by 10 cm (two segments) of the silver sorbent at 1% breakthrough. A total of 5.8 g of iodine was metered to Column I compared to 5.9 g metered to Column II before a 1% breakthrough was measured in either column. The data also indicated that the presence of airborne TBP did not have a deleterious effect on capacity of the material to retain iodine since the retention of iodine was at the stoichiometric maximum for this material.

Because TBP seemed to be having no effect on the iodine sorbent, an investigation was carried out to determine the airborne concentration in the feed stream to the columns. Past calculations of airborne TBP concentrations were done by estimating the volume loss of TBP/NPH liquid during the experiment. The PA460 analyzer was used in this investigation. The instrument was used to measure TBP in the feed stream to the column at identical conditions as those in the two experiments. An airborne TBP concentration of $\sim$10 mg/m^3 was measured. This was about one-eightieth that estimated from volume loss calculations.

A higher airborne TBP concentration was necessary for experimentation for a better simulation of actual reprocessing off-gas streams. A concentration of $\sim$1000 mg/m^3 is assumed typical in off-gas streams. Modifications were made to the TBP generator apparatus which included adding glass beads to the gas wash bottles to increase surface area for sparging. Analysis after the modifications showed a concentration of $\sim$500 mg/m^3 which was considered adequate for experimentation.

TABLE III

Analysis of Iodine Retention of 14% Ag Impregnated Iodine Sorbent

Sample	Measured % CH_3I Breakthrough (C/Cox10)	Calculated CH_3I Retention from Breakthrough Curves[a] gI/g Ag[c]	Theoretical[b] Maximum gI/g Ag
Column I			
Section A	100 (material H)	(1.3)[d]	
Section B	90 (material H)	(1.8)[d]	
Section C	84	1.1	1.2
Section D	61	0.4	
Section E	38	0.1	
Column II			
Section A	93	1.6	1.2
Section B	17	1.1	

Calculated retention at 1% breakthrough in 2 sections (10 cm) of iodine sorbent (from raw data)[a].

Column I (protection)	Column II (no protection)
5.8 gI	5.9 gI

(a) Uncertainty is ± 25% at the 95% confidence level.

(b) Based on the reaction Ag+I→AgI.

(c) Based on 7 wt% Ag.

(d) Grams of Iodine.

A third demonstration experiment was initiated in late July 1978 using the modified TBP generation apparatus. In this experiment, Column I contained two 5 cm segments of material A followed by three 5 cm segments of a commercially available 18 wt% Ag substituted mordenite iodine sorbent. Column II contained four 5 cm segments of the 18% Ag mordenite sorbent. The columns were conditioned with air at 2% relatively humidity for 20 hours followed by one hour of conditioning with air plus TBP/NPH vapor prior to metering methyl iodide into the air stream. During the experiment, average airflow was 2 ℓ/min. and average methyl iodide concentration was 160 mg/m^3.

Total methyl iodide metered to Column I was 6.75 g and to Column II was 6.11 g before the experiment was terminated. Figure 14 is the breakthrough for sections A, B, C, and D of Column I. Figure 15 is the breakthrough curve for sections A and C of Column II, and Figure 16 is the breakthrough curve for sections B and D of Column II.

To determine the effectiveness of material A to protect the silver mordenite, a comparison of breakthrough curves is made between section C in Column I and section A in Column II, and section D in Column I and section B in Column II. Table IV is a summary of the breakthrough data.

The iodine retention at a 1% breakthrough in 10 cm of Column I (sections C and D) was 30 times greater than the iodine retention in 10 cm of Column II (sections A and B). Material A protected the sorbent increasing the iodine retention. The iodine retention of the material was also significantly less than theoretical. The breakthrough for the unprotected Column I, extrapolated to C/C_o = 100%, was ∿0.7 g, which is 60% of the theoretical maximum.

EFFECT OF NO_2

The final experiment in this study was conducted in September 1978 and diverted slightly from the previous studies using the bench scale demonstration unit. In this experiment, the effects of NO_2 on iodine retention were assessed. No protective sorbent for TBP removal was used in this experiment. The protective sorbent was to be included in future studies using NO_2 in the feed stream; however, the project was terminated before additional experiments were started.

Two stainless steel columns were prepared. Both columns contained 5 cm of 7 wt% Ag silica gel iodine sorbent in five segments, the same iodine sorbent material used in the first experiment in April 1978. The columns were placed in the oven and preconditioned for 24 hours with air at 2% relative humidity and TBP/NPH vapor for one hour prior to metering methyl iodide. The columns were kept at 130 to 135°C throughout the experiment.

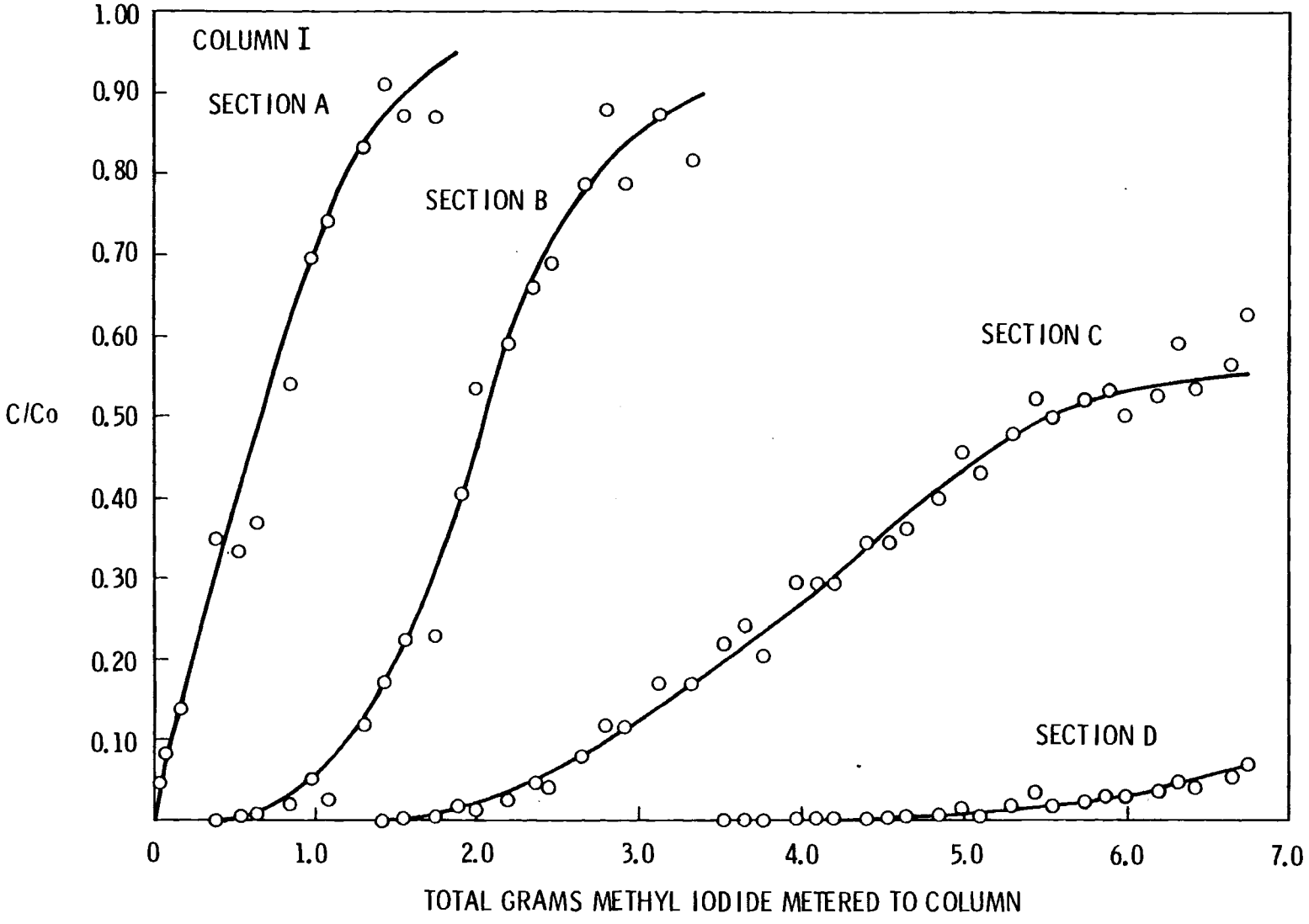

FIGURE 14. Breakthrough History for Methyl Iodide Loading onto Column I.

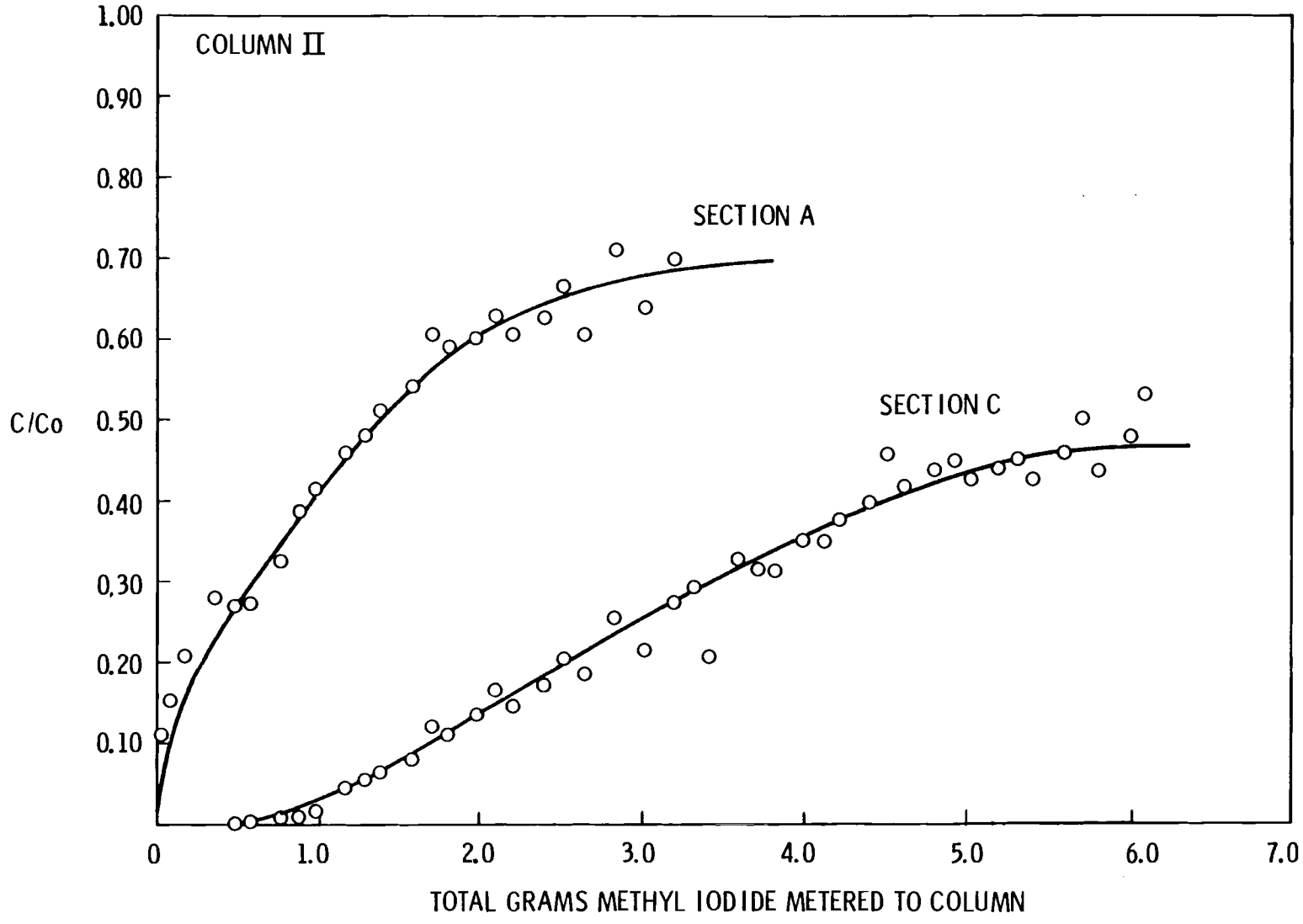

FIGURE 15. Breakthrough History for Methyl Iodide Loading onto 18 wt% Ag Substituted Mordenite, Column II, Sections A and C.

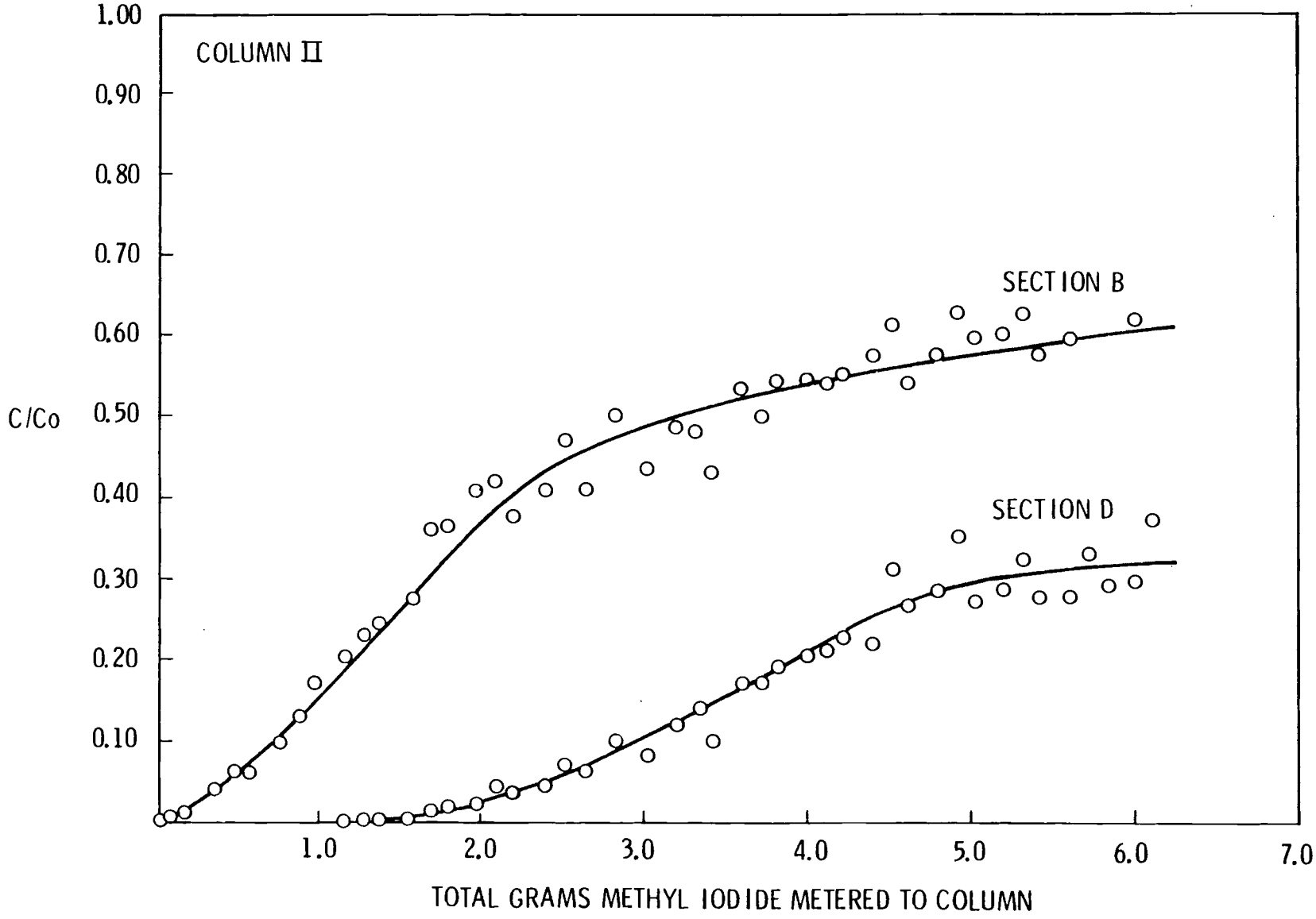

FIGURE 16. Breakthrough History for Methyl Iodide Loading onto 18 wt% Ag Substituted Mordenite, Column II, Sections B and D.

TABLE IV

Analysis of Iodine Retention of 18% Ag Substituted Mordenite Iodine Sorbent

Sample	Measured % CH_3I Breakthrough ($C/C_o \times 100$)	Calculations From Breakthrough Curves[a] gI/g Ag	Theoretical Maximum[b] gI/g Ag
Column I			
Section A	90	(1.3)[c]	
Section B	82	(1.25)[c]	
Section C	55	0.4	1.2
Section D	7	0.2	
Section E	None	<0.1	
Column II			
Section A	65	0.4	1.2
Section B	60	0.2	
Section C	45	0.2	
Section D	30	0.1	

Calculated iodine retention at 1% breakthrough in 2 sections of silver sorbent (from raw data)[a].

Column I (protection)	Column II (no protection)
4.4 g	0.14 g

(a) Uncertainty ± 25% at a 95% confidence level

(b) Based on reaction Ag+I→AgI

(c) Grams of Iodine

Methyl iodide was metered along with TBP/NPH vapor laden air flowing at 1.95 ℓ/min. until a total of 6.66 g was loaded onto each column. Approximate methyl iodide concentration was 200 mg/m^3 and approximate TBP vapor concentration was 500 mg/m^3.

Breakthrough curves for each column were constructed from the data. Figure 17 is the breakthrough for Column I and Figure 18 is the breakthrough curve for Column II. Iodine retention calculations are given in Table V. As in the first experiment in this bench scale demonstration series, the

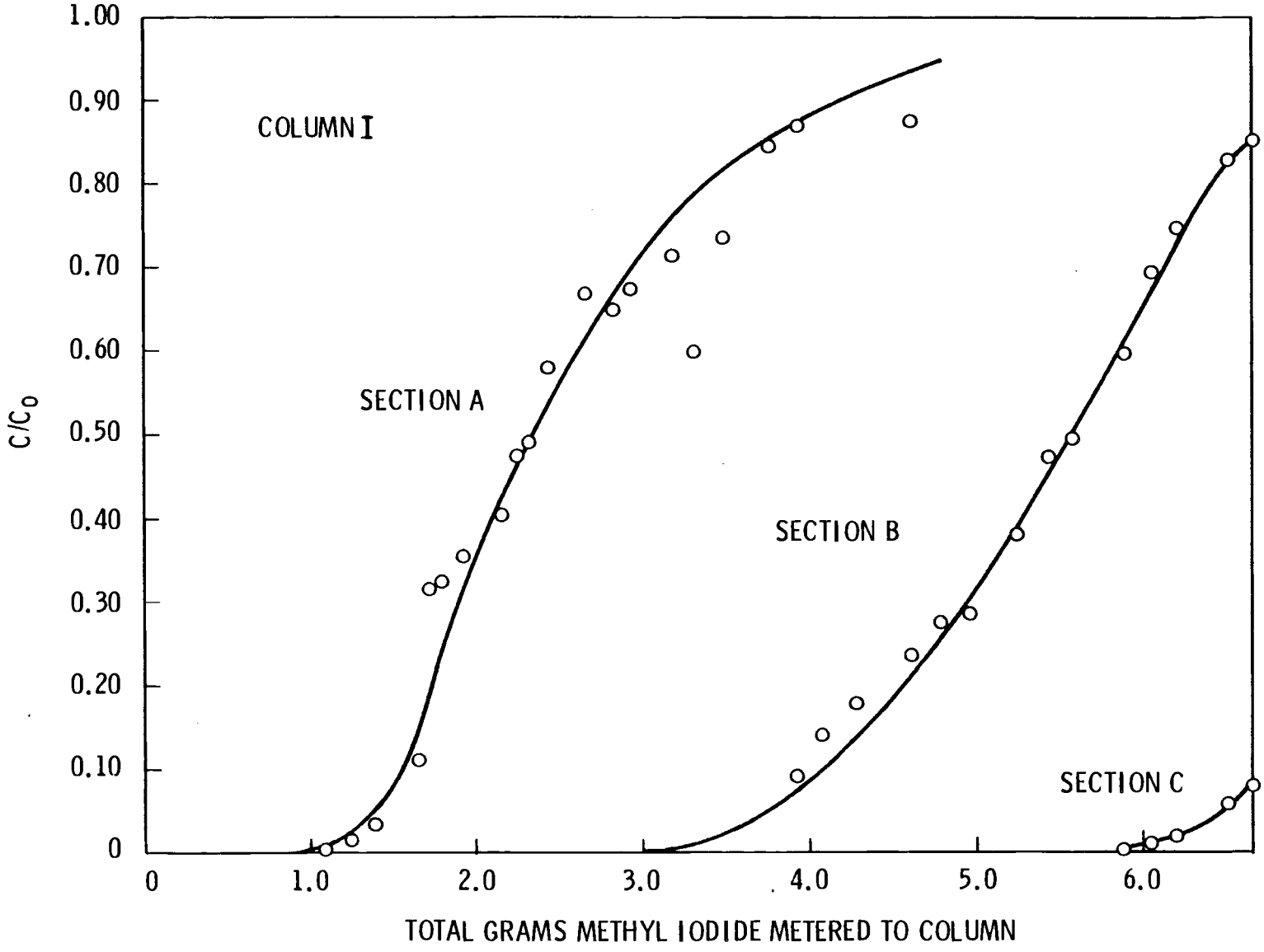

FIGURE 17. Breakthrough History for Methyl Iodide Loading onto 7 wt% Ag Impregnated Silica Gel Sorbent, Column I.

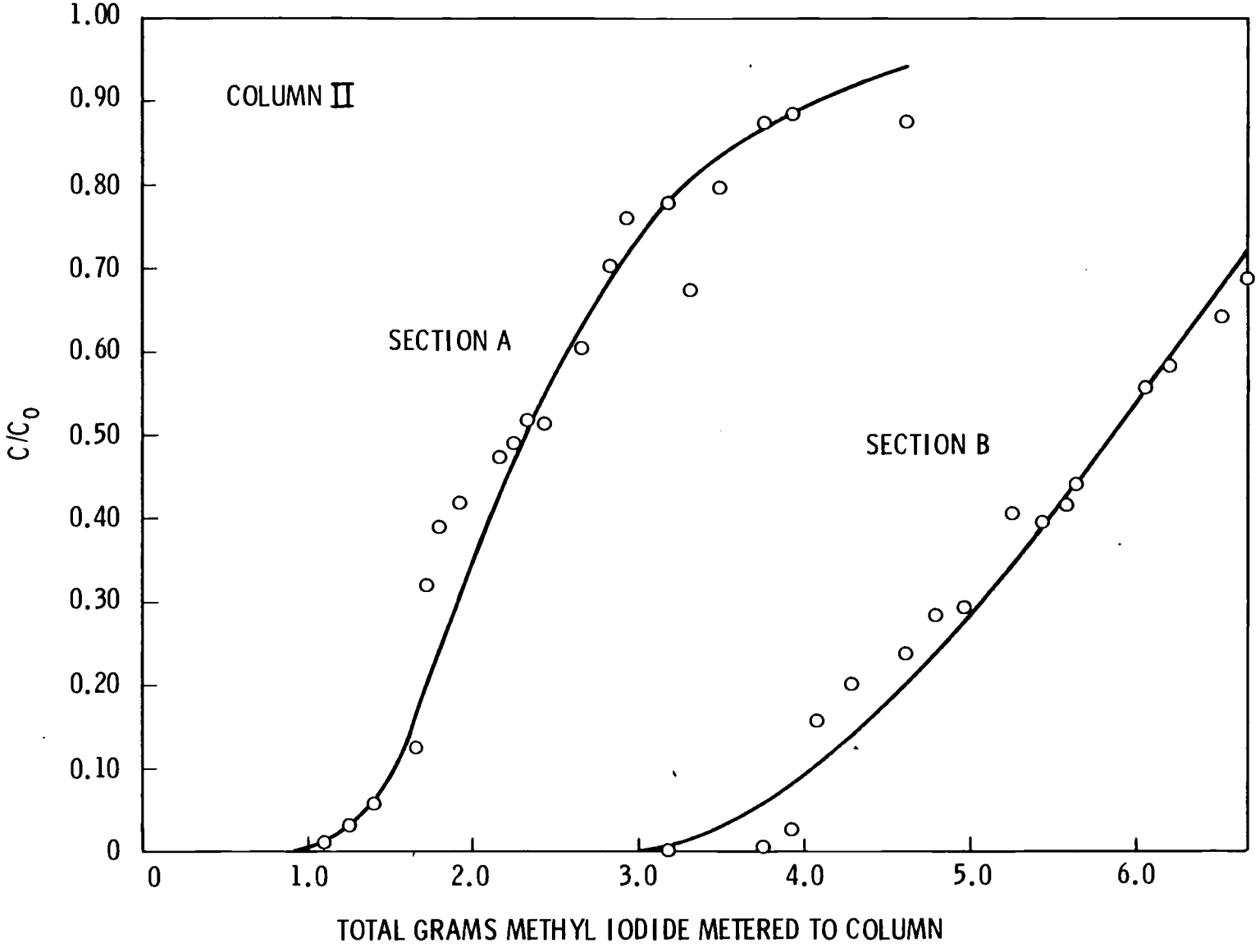

FIGURE 18. Breakthrough History for Methyl Iodide Loading onto 7 wt% Ag Impregnated Silica Gel Sorbent, Column II.

TABLE V

Analysis of Iodine Retention of 7% Ag Iodine Sorbent Prior to Introducing NO_2

Sample	Measured % CH_3I Breakthrough (C/C_o x 100)	Calculated Ch_3I Retention From Breakthrough Curves[a] gI/g Ag[c]	Theoretical Maximum[b] gI/g Ag
Column I			1.2
Section A	100	1.8	
Section B	100	1.8	
Section C		0.7	
Section D	0	-	
Section E	0	-	
Column II			1.2
Section A	100	1.8	
Section B	100	1.8	
Section C		1.2	
Section D	0	-	
Section E	0	-	

(a) Uncertainty is ±25% at the 95% confidence level

(b) Based on the reaction Ag+I→AgI

(c) Based on 7 wt% Ag

TBP had no effect on the total loading of iodine on the 7% Ag silica gel sorbent even though the TBP vapor concentration was increased. Calculated loading was greater than the stoichiometric maximum in both columns.

The material from Column I was removed, examined and photographed to note the changes that occurred. The original material was white and beaded. At the end of the iodine loading the material in the first two 5 cm sections of Column I was a light yellow mixed with a few black beads, the third 5 cm section was about an equal mixture of yellow and grey-black

beads and the last two sections were entirely black. This was expected since the first two sections were saturated with iodine and the yellow is a characteristic color of AgI. The middle section was only partially loaded with iodine, confirmed by the mix of yellow and black colored beads. The last two sections had not "seen" any iodine and were black. The black color is a characteristic of silver oxide formed by reaction of the sorbent with the air and/or TBP/NPH vapor. The material in all segments was free-flowing and no organic residue could be visually detected, although the odor of TBP was noticeable in all segments.

Column II was left in the oven at 130 to 135°C. Dry air containing ~2% NO_2 only was then metered to the column at 1.9 ℓ/min. for 45 hours. This concentration of NO_2 was in the range expected in actual reprocessing off-gas streams.[2] This was done to determine the effect the NO_2 had on the iodine sorbent after being loaded with iodine in the presence of TBP/NPH. It has been postulated that NO_2 in an air stream containing TBP/NPH will counter-act the deleterious effects of the TBP on the 7% Ag silica gel sorbent by some uncertain mechanism.[1] It was assumed that Column II looked the same as Column I (which was removed) before introducing the NO_2.

At the end of 45 hours, the material in Column II was examined and photographed. The first two 5 cm segments were all white and resembled the virgin material. The third 5 cm segment was nearly all white with a thin layer of yellow near the bottom (downstream) of the segment. The last two segments were a pure light yellow; this as noted earlier is characteristic of silver iodide. It appears that the iodine loaded onto the first two segments of Column II was "washed" onto the last two segments of the column by the NO_2, leaving the iodine sorbent in the original white state (regenerated). This was not expected. Rather, it was assumed that the first two segments of Column II would remain loaded with iodine and be the characteristic yellow color. It was also expected that any of the material not loaded with iodine (the material that was dark) would be regenerated to the white color of the virgin material. The silver on the silica gel would be reduced to the ionic (original) $AgNO_3$ state from the oxide (black) state by the NO_2.

Confirmation that the iodine was washed onto the last two segments would require analysis of the last two column sections to determine iodine content. This could be done by x-ray fluorescence of the crushed silica sorbent. However, the program was terminated before further research could be conducted.

CONCLUSIONS

Even though the research program was not carried to completion with full scale demonstration of an air cleaning process, the work that was completed gave some significant data. The studies did answer questions that were either stated or implied in the beginning of the program. The conclusions drawn from the completed work are given below.

- It is possible to quantitatively analyze low concentrations of airborne TBP using a modified real time continuous instrument. Based on vapor pressure calculations, concentrations as low as 0.12 mg/m^3 were measured using this instrument.
- Airborne TBP vapor can be retained by commercially available inorganic solid sorbent material. The highest retention of the materials studied was found in an alumina catalyst (material A). The retention capacity before detectable breakthrough of this material was great enough that it could be used in actual air cleaning systems. This material is similar to the iodine sorbent materials used in gas cleaning and would therefore be compatible with proposed material handling techniques for full scale reprocessing plants.
- Neither the 7 wt% Ag or 14 wt% Ag commercial silica gel iodine sorbent was affected by airborne TBP at concentrations used. In three experiments using TBP vapor at concentrations as high as 500 mg/m^3 the stoichiometric maximum amount of iodine at saturation (100% breakthrough) was retained by columns of the material kept at 130 to 135°C. In some cases greater than the stoichiometric amount of iodine calculated from

breakthrough data was retained by the silica gel sorbent at saturation. Because of this, the iodine sorbent material could be used in actual process streams containing <500 mg/m^3 TBP without treating the off-gas to remove the TBP.

- The presence of airborne TBP vapor at a concentration of 500 mg/m^3 reduced the capacity of a commercially available 18 wt% Ag substituted mordenite iodine sorbent to retain iodine by 60% (compared to stoichiometric retention). This material could not be used efficiently in actual process off-gas streams without pretreatment to remove TBP. Furthermore, material A was demonstrated to be an effective sorbent for TBP and protect the 18 wt% Ag mordenite iodine sorbent downstream. Protected columns were able to retain 30 times more TBP than unprotected columns.
- Visual examination of 7 wt% Ag sorbent loaded with iodine in presence of TBP/NPH and then subjected to 2 volume % NO_2 in air indicated that the NO_2 will regenerate the sorbent. The iodine appeared to wash off the material and leave the material in the original state. This would be undesirable in an actual process stream containing NO_2. It is necessary to irreversibly trap the iodine in a stable matrix. Additional analytical work is needed to confirm this conclusion.

This study generated many questions. These include, why did the TBP/NPH vapor have no deleterious effect on the iodine retention of the 7% and 14% Ag silica gel sorbents at concentrations of ∿500 mg/m^3 yet had definite deleterious effect on the 18 wt% Ag mordenite sorbent? Also, why was iodine retained by the 7 wt% and 14 wt% Ag sorbent at greater than stoichiometric amounts? And, why did the NO_2 appear to regenerate the upstream segments of the 7 wt% Ag silica gel iodine sorbent that were saturated with iodine and wash this iodine onto the downstream 7 wt% Ag sorbent? These and other questions would require additional research in an extended research program.

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APPENDIX A

PROPERTIES OF TBP SORBENT MATERIALS

Material	Chemical Composition	Size	Nature	Surface Area m2/g	Pore Diameter A	Density lbs/ft^3
Charcoal	C	6x14 mesh	irregular	-	-	55
A	Al_2O_3 92%	6x14 mesh	granular	210	35-45	30
B	Al_2O_3 50%	3/16"x3/16"	cylinder	100	-	36
C	Al_2O_3 99%	1/16"	extrudate	215	150	50
D	-					
E	-	1/4"x1/3"	bead	70	-	63
F	Al_2O_3 25%, SiO_2 75%	3/16"x3/16"	cylinder	-	-	46
G	SiO_2 84%, MgO 15%	16x30 mesh	irregular	298		53
H	Carbon + Other unknown inorganics	-	irregular	-	-	34
J	Lead subsituted zeolite	8x14 mesh	beads	-	-	91
K	SiO_2 68%, Al_2O_3 12%, Fe_2O_3 5%, MgO 10%	8x16 mesh	irregular	125	-	28-36
L	SiO_2 68%, Al_2O_3 12%, Fe_2O_3 5%, MgO 10%	8x30 mesh	irregular	125	-	33-36
M	SiO_2 68%, Al_2O_3 12%, Fe_2O_3 5%, MgO 10%	12x45 mesh	irregular	125	-	29-33

APPENDIX B

WEIGHT OF MATERIALS USED IN INITIAL SCREENING STUDIES

Material	Weight of Material Packed Into 25 cm Diameter Stainless Steel Column -- g
Charcoal	16.726
A #1	32.51
#2	31.899
B	26.809
C	10.475
D	24.58
E	29.527
F	21.386
G	16.96
H	15.768
J	42.622
K	18.786
L	19.638
M	21.85

APPENDIX C

WEIGHT OF MATERIAL USED IN BENCH SCALE DEMONSTRATION STUDIES

Experiment #1

Section	Column I (7 wt% Ag iodine sorbent) g	Column II g	
A	19.72	31.19	(material A)
B	19.94	31.27	(material A)
C	19.54	19.79	(7 wt% Ag sorbent)
D	19.96	19.86	(7 wt% Ag sorbent)
E	20.56	19.84	(7 wt% Ag sorbent)

Experiment #2

Section	Column I g	Column II (14 wt% Ag iodine sorbent) g
A	30.76 (material A)	21.16
B	31.15 (material A)	21.97
C	22.15 (14 wt% Ag sorbent)	19.74
D	21.82 (14 wt% Ag sorbent)	21.90
E	22.09 (14 wt% Ag sorbent)	21.98

Experiment #3

Section	Column I g	Column II (18 wt% Ag iodine sorbent) g	
A	31.61 (material A)	29.75	
B	31.43 (material A)	29.32	
C	29.46 (18 wt% Ag sorbent)	30.34	
D	29.70 (18 wt% Ag sorbent)	30.24	
E	30.05 (18 wt% Ag sorbent)	22.19	(7 wt% Ag sorbent)

Experiment #4 (effects of NO_2)

Section	Column I (7 wt% Ag iodine sorbent) g	ColumnII (7 wt% Ag iodine sorbent) g
A	19.32	18.98
B	19.27	20.01
C	18.83	19.04
D	17.38	18.73
E	19.51	19.55

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